Organometallics **2001**, *20,* 1115−1127

Synthesis and Oxidation of Dirhenium C_4, C_6, and C_8 Complexes of the Formula $(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)(C{\equiv}C)_n(R_3P)(ON)Re(\eta^5\text{-}C_5Me_5)$ (R = 4-C_6H_4R', c-C_6H_{11}): In Search of Dications and Radical Cations with Enhanced Stabilities†

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Received November 13, 2000

The racemic methyl complexes $(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)(CH_3)$ (R: **b**, 4-$C_6H_4CH_3$; **c**, 4-C_6H_4-*t*-C_4H_9; **d**, 4-$C_6H_4C_6H_5$; **e**, c-C_6H_{11}), which feature phosphines that are more electron rich and/or bulkier than $P(C_6H_5)_3$, are elaborated by reactions with $HBF_4{\cdot}OEt_2$/chlorobenzene, HC≡CH or HC≡CC≡CSiMe$_3$, and *t*-BuOK to give the alkynyl complexes $(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)(C{\equiv}CH)$ (**3b**,**c**) and $(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)(C{\equiv}CC{\equiv}CSiMe_3)$ (**7b**−**e**). The latter are converted (K_2CO_3/MeOH or wet *n*-$Bu_4N^+F^-$) to butadiynyl complexes (**8b**−**e**). Homo- or cross-couplings (**3b**, **8b**−**e**; $Cu(OAc)_2$/pyridine) lead to the μ-butadiynediyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)(C{\equiv}C)_n(R_3P)(ON)Re(\eta^5\text{-}C_5Me_5)$ (**4b**; $n = 2$) and analogous μ-hexatriynediyl (**10b**; $n = 3$) and μ-octatetraynediyl (**9b**−**e**; $n = 4$) species. Oxidation of **4b** by $AgSbF_6$ (ca. 1:1 or 1:2) gives the radical cation $\mathbf{4b}^{\bullet+}SbF_6^-$ or the dication $\mathbf{4b}^{2+}(SbF_6^-)_2$. These isolable compounds exhibit delocalized mixed-valence and cumulenic electronic ground states, respectively. The cyclic voltammograms of **9b**−**e** and **10b** show oxidations to analogous species, with much better chemical reversibilities than for the $P(C_6H_5)_3$ analogues. However, these longer chain systems decompose rapidly at −78 °C and could not be isolated or spectroscopically characterized.

Introduction

Over the past decade, complexes in which sp carbon chains span two transition metals have captured the attention of many researchers.[2−11] Much of this interest has been prompted by the promise of useful materials properties, most of which are connected to charge-transfer phenomena between the metal termini. As such, this field has evolved on three broad fronts. First, it was necessary to develop synthetic methods for constructing the carbon/metal skeleton. This proved to be rather straightforward for neutral 18-valence-electron complexes with $(C{\equiv}C)_n$ or μ-polyynediyl linkages. Such MC_4M or μ-butadiynediyl systems are now commonplace. Bridges that are longer than eight carbons present additional challenges,[8−10] but even here the number of examples can be expected to grow rapidly.

A second front has been the redox characterization of these complexes.[3−7] Physical or materials properties of interest are often associated with specific oxidation states. Scheme 1 shows the five—a "consanguineous" series[3e,6,7]—that have so far come into play (**A**−**E**). It should be emphasized that, in each case, there are

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(2) Reviews covering aspects of this field: (a) Akita, M.; Moro-oka, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 420. (b) Bruce, M. I. *Coord. Chem. Rev.* **1997**, *166*, 91. (c) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178*−*180*, 427.

(3) FeC_xFe complexes (x = 4, 8) isolable in multiple oxidation states: (a) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129. (b) Coat, F.; Lapinte, C. *Organometallics* **1996**, *15*, 477. (c) Coat, F.; Guillevic, M.-A.; Toupet, L.; Paul, F.; Lapinte, C. *Organometallics* **1997**, *16*, 5988. (d) Le Narvor, N.; Lapinte, C. *C. R. Acad. Sci. Paris, Ser. IIc* **1998**, 745. (e) Guillemot, M.; Toupet, L.; Lapinte, C. *Organometallics* **1998**, *17*, 1928. (f) See also: Coat, F.; Guillemot, M.; Paul, F.; Lapinte, C. *J. Organomet. Chem.* **1999**, *578*, 76.

(4) RuC_4Ru complexes isolable in multiple oxidation states: (a) Bruce, M. I.; Low, P. J.; Costuas, K.; Halet, J.-F.; Best, S. P.; Heath, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 1949. (b) See also: Ren, T.; Zou, G.; Alvarez, J. C. *J. Chem. Soc., Chem. Commun.* **2000**, 1197.

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(7) FeC_4Re complexes isolable in multiple oxidation states: Paul, F.; Meyer, W. E.; Toupet, L.; Jiao, H.; Gladysz, J. A.; Lapinte, C. *J. Am. Chem. Soc.* **2000**, *122*, 9405.

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Scheme 1. Representative Redox States for Complexes in Which Even-Carbon Chains Span Two Metals

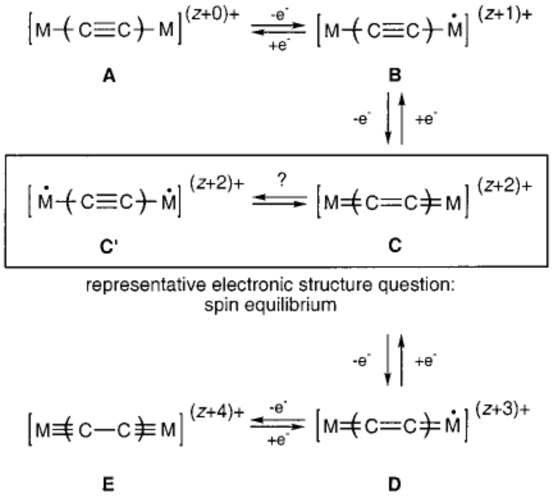
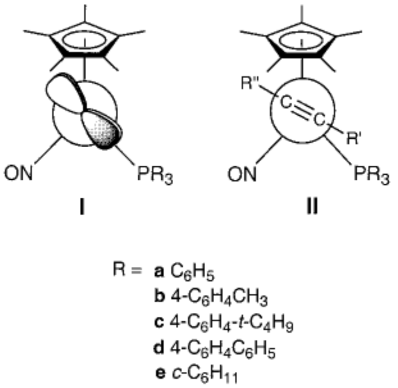


Chart 1. Newman-Type Projections[a]



[a] Legend: (I) the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)]$ with d-orbital HOMO; (II) the corresponding π-alkyne complexes.

subtle issues of electronic structure. Hence, the formulations in Scheme 1 are arbitrary, and only for **C**/**C′** are two alternatives illustrated. The accessibility of oxidation states is easily screened by cyclic voltammetry. However, many questions can only be addressed with isolated complexes. Only two systems are known to date that give *more* than three isolable oxidation states.[3e,4a]

Accordingly, a third front has been the optimization of metal end groups to support a broader range of oxidation states. This has been a major aspect of the elegant diiron and diruthenium MC_xM chemistry developed by Lapinte and Bruce.[3,4a] With regard to our signature end group, the 16-valence-electron chiral rhenium Lewis acid $[(\eta^5\text{-}C_5Me_5)Re(NO)(P(C_6H_5)_3)]^+$ (**Ia**), we were able to isolate three ReC_4Re oxidation states: the neutral μ-butadiynediyl system **A**, the radical cation **B**, and the cumulated dication **C**.[6] Rhenium–carbon multiple bonding increases with each oxidation and involves the high-lying d orbital shown in Chart 1. However, when the polyynediyl chain was extended, even to six carbons, the oxidized counterparts became dramatically less stable.[8]

We have therefore sought analogues of the end group **Ia** that would give more stable oxidation products. Our data suggested that radical cation decomposition involved chain/chain coupling and possibly atom abstraction from the solvent.[8] One obvious countermeasure would be to utilize phosphines that are more electron releasing than triphenylphosphine. The enhanced rhenium basicity should lead to thermodynamically more favorable oxidations and $E°$ values and stronger rhenium–carbon multiple bonding. From linear free energy considerations, the rates of coupling or atom abstraction should decrease. Another approach would involve bulkier phosphines, which should sterically inhibit all types of bimolecular reactions.

In our previous papers,[12,13] we reported several modified methyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PR_3)(CH_3)$ (**1**) containing phosphines that are more electron releasing and/or bulkier than triphenylphosphine. Each represents a possible building block for new families of ReC_x-Re complexes. Cyclic voltammetry verified that all of these complexes were more easily oxidized than the parent compound $(\eta^5\text{-}C_5H_5)Re(NO)(P(C_6H_5)_3)(CH_3)$ (**1a**). One radical cation was even stable enough to be crystallized and structurally characterized. Accordingly, we thought there would be an excellent chance that C_6 and C_8 complexes with such end groups would be isolable in multiple oxidation states.

In this paper, we describe second-generation C_6 and C_8 complexes in which the triphenylphosphine (**a**) of end group **Ia** has been replaced by tri-*p*-tolylphosphine (**b**), tris(*p*-*tert*-butylphenyl)phosphine (**c**), tris(*p*-phenylphenyl)phosphine (**d**), and tricyclohexylphosphine (**e**). For comparison purposes, a new C_4 system has also been synthesized. The latter is, like the triphenylphosphine analogue, isolable in three oxidation states. The C_6 and C_8 complexes undergo electrochemical oxidations with greatly improved reversibilities. However, product isolation remains problematic, indicating a need for third-generation approaches. Regardless, new homologous series of ReC_xRe complexes, differing only in the stereoelectronic properties of the phosphine ligands, are now available for study.[14]

Results

Neutral C_4 Complexes. The racemic tri-*p*-tolylphosphine methyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4\text{-}CH_3)_3)(CH_3)$ (**1b**) and the tris(*p*-*tert*-butylphenyl)phosphine homologue $(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4\text{-}t\text{-}C_4H_9)_3)(CH_3)$ (**1c**) were prepared as previously reported.[12] As shown in Scheme 2, chlorobenzene solutions were cooled to −45 °C, and $HBF_4{\cdot}OEt_2$ was added to generate labile chlorobenzene complexes.[15] Acetylene gas was bubbled through the solutions, which were warmed to 80 °C. Workups gave the π-ethyne complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)(HC{\equiv}CH)]^+BF_4^-$ (**2b**,**c**$^+BF_4^-$) as air-stable powders in 75–80% yields. Subsequent deprotonations with *t*-BuOK (−80 °C) gave the corresponding σ-ethynyl complexes $(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)(C{\equiv}CH)$ (**3b**,**c**) as orange powders in 67–95% yields.

As summarized in the Experimental Section, **2b**,**c**$^+$-BF_4^-, **3b**,**c**, and all other new diamagnetic compounds

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[12] Meyer, W. E.; Amoroso, A. J.; Jaeger, M.; Le Bras, J.; Wong, W.-T.; Gladysz, J. A. *J. Organomet. Chem.* **2000**, *616*, 44.

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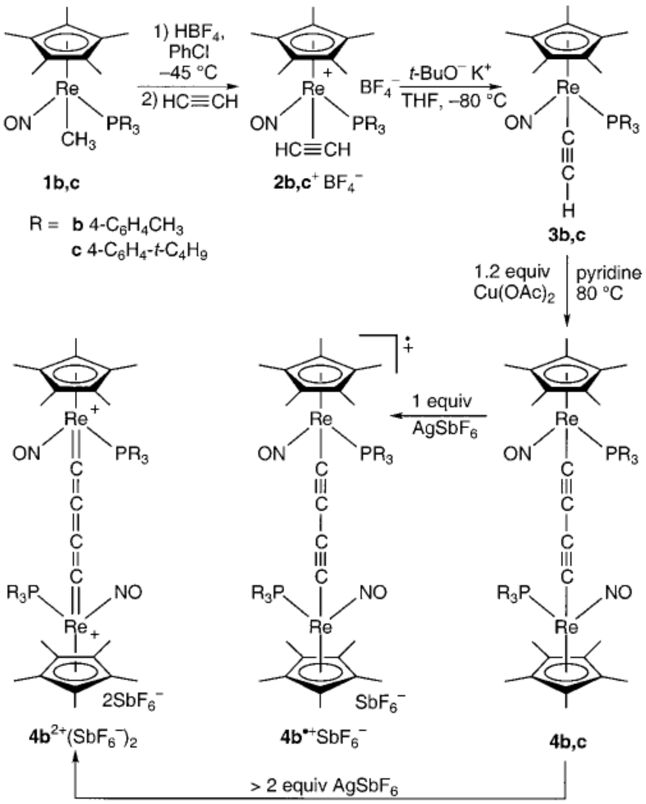
[15] Kowalczyk, J. J.; Agbossou, S. K.; Gladysz, J. A. *J. Organomet. Chem.* **1990**, *397*, 333.

Scheme 2. Syntheses of ReC_4Re Complexes



were characterized by IR, NMR (^1H, ^{13}C, ^{31}P), and mass spectrometry. Most gave correct microanalyses, but solvates were often encountered, and a few did not (e.g., $\mathbf{2c}^+BF_4^-$ from these four compounds). Since the spectroscopic properties of $\mathbf{2b,c}^+BF_4^-$, **3b**,**c**, and other monorhenium π-alkyne and σ-alkynyl complexes below closely resemble those of the triphenylphosphine analogues, they are not discussed or analyzed. However, the ^1H and ^{13}C NMR spectra are richly featured. For example, π-alkyne complexes of **I** adopt the Re−(C═C) conformation shown in **II** (Chart 1),[16] and rotation about this axis is slow on the NMR time scale. On the basis of previously established coupling constant relationships,[16,17] signals of the ═CH groups anti and syn to the PR_3 ligands in $\mathbf{2b,c}^+BF_4^-$ could be assigned (Experimental Section).

As shown in Scheme 2, **3b** and $Cu(OAc)_2$ (1.2 equiv) were reacted in pyridine at 80 °C. Workup gave the air-stable orange μ-butadiynediyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4CH_3)_3)(C{\equiv}CC{\equiv}C)((4\text{-}H_3CC_6H_4)_3P)(ON)Re(\eta^5\text{-}C_5Me_5)$ (**4b**) in 70% yield. NMR spectra showed two closely spaced sets of signals, indicative of a 58:42 mixture of configurational diastereomers. Crystallization from CH_2Cl_2/hexane gave a diastereomerically enriched sample (75:25). Spectroscopic properties are analyzed in the following section. Under similar conditions, **3c** did not give complete coupling to **4c**, probably due to steric effects encountered in other contexts below. The corresponding tricyclohexylphosphine complex **3e** was similarly synthesized but gave no detectable coupling and was, therefore, only partially characterized. It remains possible that other recipes might better transform **3c**,**e** to μ-butadiynediyl complexes, but none were investigated.

Table 1. Summary of Cyclic Voltammetry Data[a]

complex	$E_{p,a}(1)$ $E_{p,a}(2)$	$E_{p,c}(1)$ $E_{p,c}(2)$	$E°(1)$ $E°(2)$	$\Delta E°(1)$ $\Delta E°(2)$	$i_{c/a}$	K_c[b]
4a	0.05	−0.04	0.01	90	1	1.1×10^9
	0.58	0.49	0.54	90	1	
4b	−0.17	−0.26	−0.22	90	1	1.1×10^9
	0.36	0.27	0.31	90	1	
10a	0.14	0.07	0.10	70	1	3.0×10^6
	0.52	0.45	0.48	70	1	
10b	0.06	−0.02	0.02	80	1	4.4×10^6
	0.46	0.37	0.41	90	1	
9a	0.27	0.20	0.24	70	<1	5.9×10^4
	0.56	0.49	0.52	70	<1	
9b	0.20	0.12	0.16	80	1	8.8×10^4
	0.49	0.41	0.45	80	1	
9c	0.22	0.14	0.18	80	1	1.3×10^5
	0.51	0.44	0.48	70	<1	
9d	0.31	0.18	0.25	130	<1	8.8×10^4
	0.58	0.49	0.54	90	1	
9e	0.15	0.07	0.11	80	1	2.8×10^5
	0.47	0.39	0.43	80	1	

[a] In CH_2Cl_2 at a scan rate of 100 mV/s; $E°$ vs SCE (ferrocene = 0.46 V). All E values are given in V, and all ΔE values are given in mV. [b] Comproportionation constant; $\ln(K_c) = nF(E°(2) - E°(1))/RT = 39.25(E°(2) - E°(1))$ at 22.5 °C.

As shown in Figure 1, a cyclic voltammogram of **4b** was recorded in CH_2Cl_2 (red trace, top panel). Two chemically reversible one-electron oxidations were observed ($\Delta E_p = 90$ mV; i_a/i_c ratio unity) prior to reaching the solvent-imposed anodic limit. No reductions occurred in scans to the opposite cathodic limit (−1.1 V). The $E°_1$ and $E°_2$ values, and related data, are summarized in Table 1. Importantly, each oxidation is 230 mV more facile than that of the triphenylphosphine analogue **4a** (black trace, Figure 1). Thus, preparative syntheses of the corresponding radical cation and dication—a new consanguineous family—could be undertaken with confidence, with the expectation of enhanced stabilities.

Oxidized C_4 Complexes. As shown in Scheme 2, **4b** (58:42 diastereomer mixture) and 2.8 equiv of $AgSbF_6$ were combined in toluene. Workup gave the air-stable deep blue dicationic μ-butatrienediylidene complex $\mathbf{4b}^{2+}(SbF_6^-)_2$ in 75% yield as an analytically pure solvate and a 53:47 diastereomer mixture. The ^1H and ^{31}P NMR spectra showed signals similar to the triphenylphosphine analogue $\mathbf{4a}^{2+}(PF_6^-)_2$. However, a ^{13}C NMR spectrum of a saturated CD_2Cl_2 solution did not give observable Re═C═C signals. Low-temperature NMR spectra of $\mathbf{4a}^{2+}(PF_6^-)_2$ showed additional Re═C geometric isomers,[6] but no studies of these equilibria were made here. All samples of $\mathbf{4b}^{2+}(SbF_6^-)_2$ were ESR-silent (e.g., CH_2Cl_2 solutions). There was no evidence for a low-lying triplet excited state, which would have $^{\bullet+}ReC{\equiv}CC{\equiv}CRe^{\bullet+}$ character (see **C**/**C′**, Scheme 1) and precedent in some of Lapinte's FeC_4Fe complexes.[3a]

Next, **4b** and 1.25 equiv of $AgSbF_6$ were similarly reacted. Workup gave the paramagnetic radical cation $\mathbf{4b}^{\bullet+}SbF_6^-$ as a deep green analytically pure solvated powder in 70% yield. Solid $\mathbf{4b}^{\bullet+}SbF_6^-$ was stable for weeks under an inert atmosphere at −10 °C. However, CH_2Cl_2 solutions showed some decomposition after several hours at room temperature. Crystallizations were attempted using an extensive range of solvent

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[16] (a) Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1991**, *10*, 1079. (b) Ramsden, J. A.; Weng, W.; Gladysz, J. A. *Organometallics* **1992**, *11*, 3635.

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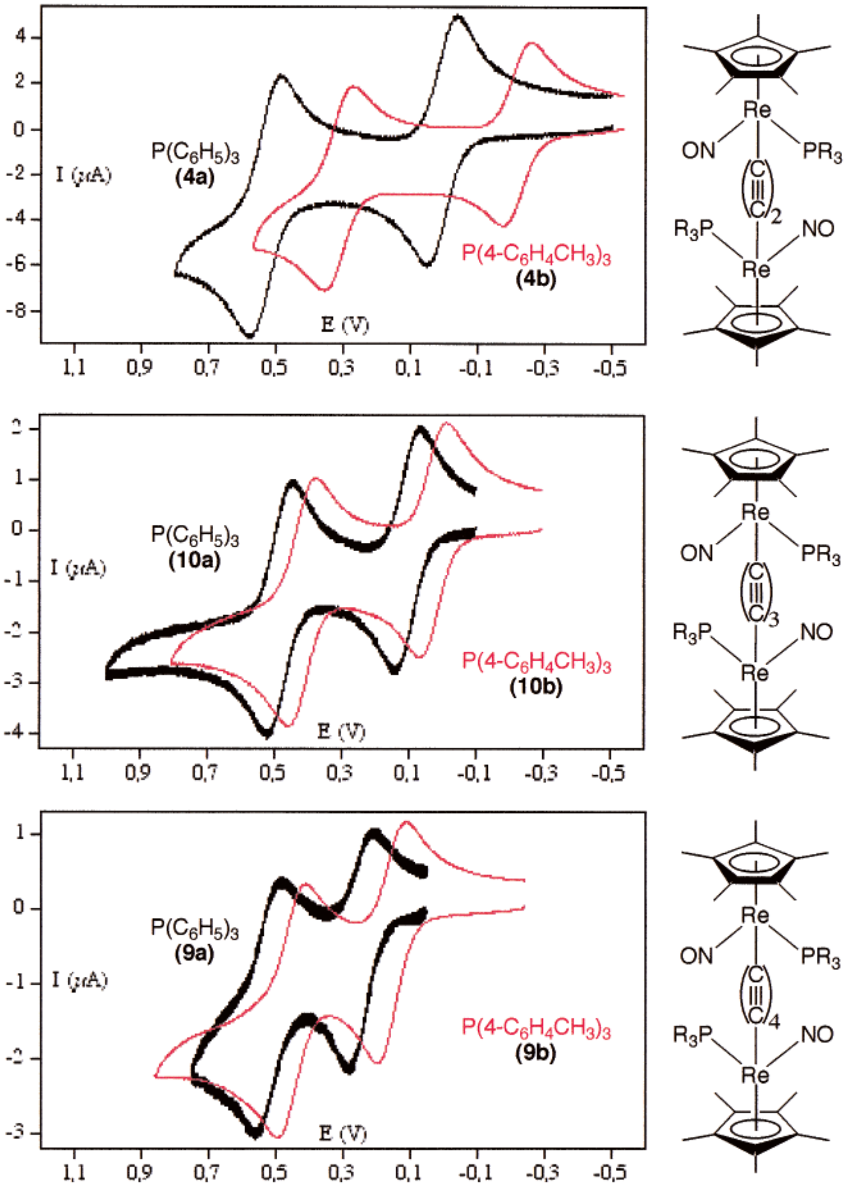

Figure 1. Cyclic voltammograms of C_4, C_6, and C_8 complexes.

combinations, mixing techniques, and temperatures. Unfortunately, only microcrystals or small needles that were unsuitable for X-ray diffraction were obtained. The corresponding hexafluorophosphate salt, which was similarly prepared but only partially characterized, gave similar results.

The radical cation $\mathbf{4b}^{\bullet+}\mathrm{SbF}_6^-$ is a mixed-valence compound, formally Re(I)/Re(II) or d^6/d^5. A variety of otherwise symmetrical bimetallic d^6/d^5 species have been studied, and they can show localized, partially delocalized, or fully delocalized electronic structures (classes I–III).[18] This issue was probed with $\mathbf{4b}^{\bullet+}\mathrm{SbF}_6^-$. First, IR spectra showed a single ν_{NO} band both in CH_2Cl_2 (1665 cm^{-1}) and in the solid state. As depicted in Figure 2, the band was between those of **4b** and $\mathbf{4b}^{2+}(\mathrm{SbF}_6^-)_2$ (1622 and 1719 cm^{-1}), indicating an intermediate level of π back-bonding, and was of comparable width. If, on the very rapid IR time scale (ca. 10^{-13} s), one rhenium end group were neutral and the other cationic, two ν_{NO} bands would be expected. Furthermore, $\mathbf{4b}^{\bullet+}\mathrm{SbF}_6^-$ exhibited only one $\nu_{C\equiv C}$ band, at a frequency lower than that of **4b** (1873 vs 1963 cm^{-1}). Therefore, the ground state of $\mathbf{4b}^{\bullet+}\mathrm{SbF}_6^-$ is best represented with a half-positive charge and half-electron on each rhenium end group.

The electronic structure of $\mathbf{4b}^{\bullet+}\mathrm{SbF}_6^-$ was further probed by ESR in CH_2Cl_2. As shown in Figure 3, an undecet with broad individual lines was observed ($g = 2.02$). The coupling or $A_{\mathrm{iso,Re}}$ value was 102 G. Rhenium has two principal isotopes of spin $^5/_2$, but the magnetic moments are very close and they can usually be treated as a single spin system. Hence, an undecet indicates that the odd electron is delocalized over both rhenium end groups on the fast ESR time scale (ca. 10^{-9} s). By comparison, the corresponding monorhenium radical cations $\mathbf{1b}^{\bullet+}\mathrm{PF}_6^-$ (generated in situ)[12] and $\mathbf{1b}^{\bullet+}\mathrm{B}(3,5\text{-}C_6H_3(CF_3)_2)_4^-$ (crystallized)[13] give sextets with $A_{\mathrm{iso,Re}}$

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(18) (a) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247. (b) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (c) Crutchley, R. J. *Adv. Inorg. Chem.* **1994**, *41*, 273. (d) Astruc, D. *Electron Transfer and Radical Processes in Transition Metal Chemistry*; VCH: New York, 1995. Part I.

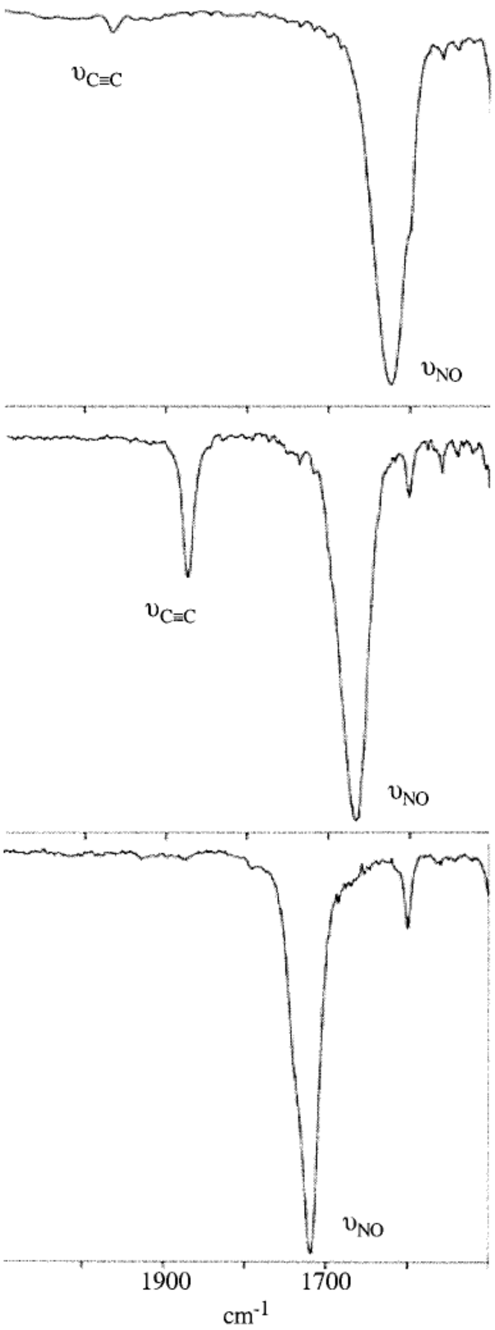

Figure 2. IR spectra of **4b** (top), $\mathbf{4b}^{\bullet+}SbF_6^-$ (middle), and $\mathbf{4b}^{2+}(SbF_6^-)_2$ (bottom).

values that are approximately twice as large.[12,13] Here, analogous electron delocalization is impossible.

The UV–visible spectra of $\mathbf{4b}^{n+}(SbF_6^-)_n$ (Experimental Section) were similar to those of the triphenylphosphine analogues $\mathbf{4a}^{n+}(PF_6^-)_n$.[6] Complex **4b** exhibited, like its monorhenium counterparts, only a featureless tail into the visible region. However, $\mathbf{4b}^{\bullet+}SbF_6^-$ gave a visible band at 452 nm (ϵ = 5800 M^{-1} cm^{-1}, CH_2Cl_2) that was absent in the monorhenium radical cations $\mathbf{1b}^{\bullet+}X^-$.[13] The various classes of mixed-valence complexes also exhibit distinguishing near-IR bands.[18] As shown in Figure 4, $\mathbf{4b}^{\bullet+}SbF_6^-$ gave unique absorptions at 891, 1020, and 1225 nm (CH_2Cl_2). The first sometimes showed fine structure or noise, and maxima were determined from curve-fitting programs. Essentially identical spectra were obtained in acetone and acetonitrile. Data are summarized in Table 2, and further interpreted below.

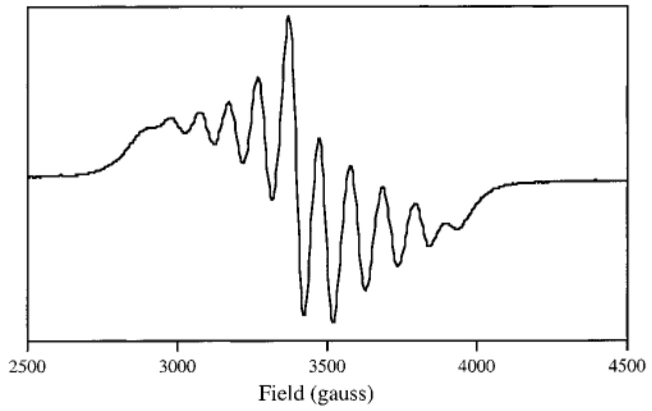

Figure 3. ESR spectrum of $\mathbf{4b}^{+\bullet}SbF_6^-$.

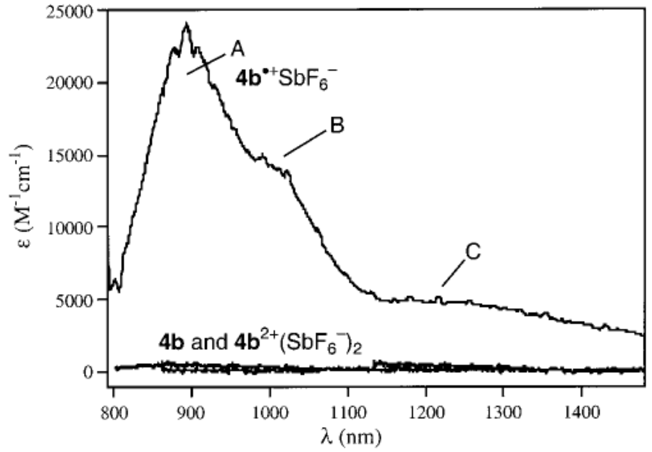

Figure 4. Near-IR spectrum of $\mathbf{4b}^{\bullet+}SbF_6^-$ (CH_2Cl_2) with background spectra of **4b** and $\mathbf{4b}^{2+}(SbF_6^-)_2$.

C_6 and C_8 Complexes. As shown in Scheme 3, chlorobenzene solutions of the methyl complexes **1b–e** were treated with $HBF_4{\cdot}OEt_2$ at −45 °C. Subsequent additions of the 1,3-diyne $HC{\equiv}CC{\equiv}CSiMe_3$ gave the π complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)(HC{\equiv}CC{\equiv}CSiMe_3)]^+BF_4^-$ ($\mathbf{6b{-}e}^+BF_4^-$) in 48–92% yields after workup. These air-stable tan powders could be stored for months at room temperature. Only the $HC{\equiv}C$ moiety coordinated, but two Re–(C≡C) rotamers were always present (see **II** in Chart 1).[16,17] Deprotonations with *t*-BuOK gave the σ complexes $(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)(C{\equiv}CC{\equiv}CSiMe_3)$ (**7b–d**) in 80–88% yields. Subsequent protodesilylations with either K_2CO_3/MeOH (**7b,e**) or wet $n\text{-}Bu_4N^+$ F^-/THF (0.2 equiv; superior for **7c,d**) gave the 1,3-butadiynyl complexes $(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)(C{\equiv}CC{\equiv}CH)$ (**8b–e**) in 61–92% yields.[19] The spectroscopic features of all of these complexes were similar to those of the triphenylphosphine analogues.

Complexes **8b–e** and $Cu(OAc)_2$ (1.1 equiv) were reacted in pyridine at 50–80 °C. Workups gave the μ-octatetraynediyl complexes $(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)(C{\equiv}C)_4(R_3P)(ON)Re(\eta^5\text{-}C_5Me_5)$ (**9b–e**) as orange or red powders in 38–54% yields. All were more soluble in nonpolar solvents than the triphenylphosphine analogue **9a**. The diastereomers of the triarylphosphine com-

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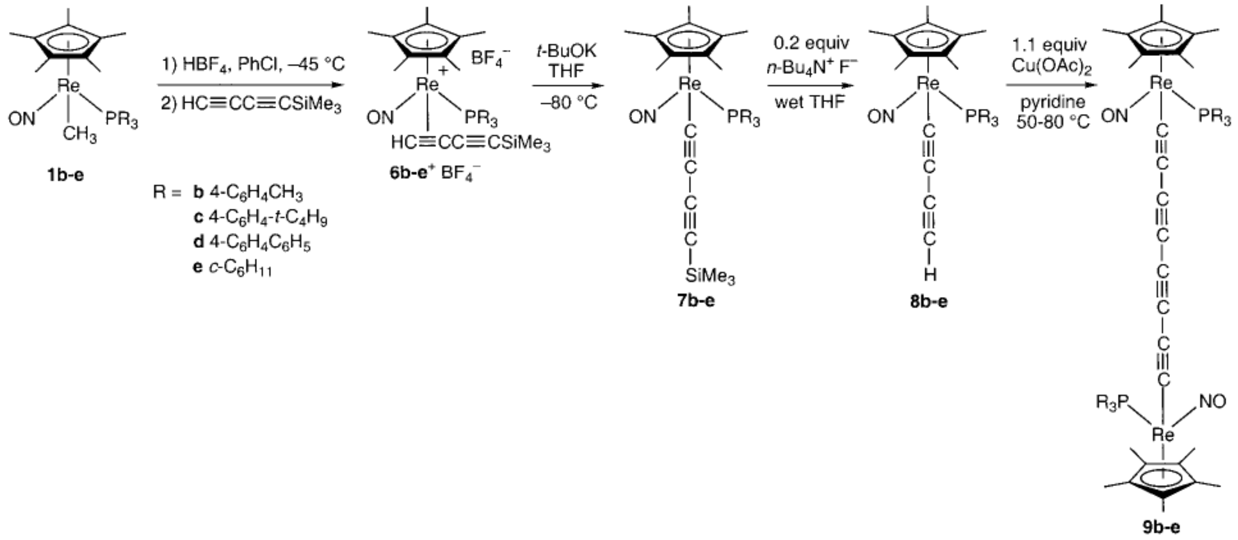
(19) Complexes **8b–d** are moderately stable toward silica and, if necessary, could be purified by a quick filtration using THF/hexane (1:1).

Table 2. Analysis of the Near-IR Spectrum of $4b^{\bullet+}SbF_6^-$ in Figure 4[a]

	λ_{max} (nm)	$\tilde{\nu}_{op}$ (cm^{-1})	ϵ_{max} (M^{-1} cm^{-1})	$\Delta\tilde{\nu}_{1/2}$ (cm^{-1})	V_{ab}, class III (cm^{-1}, eV)	V_{ab}, class II[b] (cm^{-1}, eV)	$\Delta\tilde{\nu}_{1/2(calc)}$, class II (cm^{-1})
band A	891[c]	11 200	24 000	1500	5600, 0.69	1700, 0.21	5090
band B	1020[d]	9804	14 000	1300	4900, 0.61	1100, 0.14	4760
band C	1225[e]	8160	4800	1400	4100, 0.51	600, 0.08	4340

[a] See Table 4 of ref 6 for additional background, including comments on significant digits. [b] Calculated from $(0.0205/r)(\epsilon_{max}\Delta\tilde{\nu}_{1/2}\tilde{\nu}_{op})^{1/2}$, where $r = 7.73$ Å. [c] ±3 nm. [d] ±10 nm. [e] ±30 nm.

Scheme 3. Syntheses of ReC_8Re Complexes

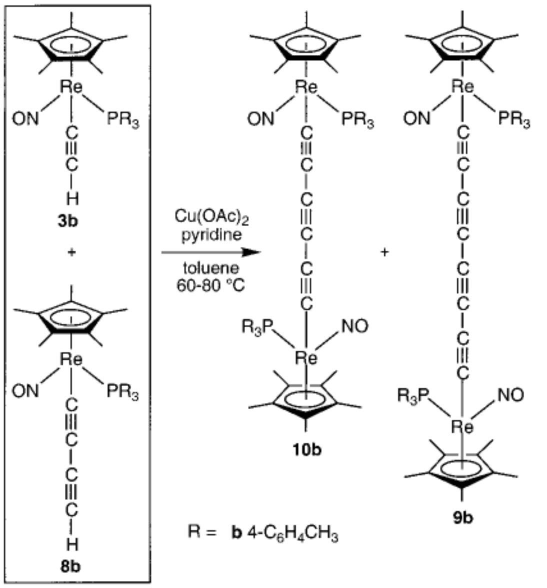


plexes **9b–d** were much easier to distinguish by NMR than for **9a**, suggesting that the larger aryl groups enhance "steric communication" between the end groups. Also, diastereomer ratios increased from 50:50 for **9b** to (75–71):(25–29) for **9c**,**d**. Attempted crystallization of **9c**,**d** gave further enrichment ((95–94):(5–6)). However, single crystals suitable for X-ray diffraction were never obtained. The tricyclohexylphosphine complex **9e** gave, under all conditions examined, a single set of NMR resonances.

In the triphenylphosphine series, co-oxidation of ethynyl and 1,3-butadiynyl complexes **3a** and **8a** gives an approximately statistical ratio of all three possible cross-coupling and homocoupling products.[8] Due to the ease of chromatographic separation, this constitutes a practical route to the μ-hexatriynediyl complex (η^5-C_5Me_5)Re(NO)($P(C_6H_5)_3$)($C{\equiv}C$)$_3$(($C_6H_5)_3P$)(ON)Re(η^5-C_5Me_5) (**10a**). As shown in Scheme 4, ethynyl and 1,3-butadiynyl complexes **3b** and **8b** were similarly reacted with $Cu(OAc)_2$ (1:1:2.5 mol ratio) in pyridine at 70 °C. Chromatography gave the target complex **10b** in 23% yield as a 50:50 diastereomer mixture (65:35 after attempted crystallization). Some C_8 homocoupling product **9b** formed, but the C_4 adduct **4b** (which would elute first) was not detected. This provides additional evidence for a steric effect of the phosphine ligand upon rates of oxidative homocouplings of ethynyl complexes **3**.

Cyclic voltammograms of **10b** and **9b** are shown in Figure 1, and data are summarized in Table 1. As found for **4b**, these complexes are thermodynamically easier to oxidize than the triphenylphosphine analogues **10a** and **9a** (red vs black traces). The differences (80 mV for $E°_1$, 70 mV for $E°_2$) are less than with **4b**, as might be intuitively expected from the longer chain length. Furthermore, the chemical reversibility is markedly improved. Data for **9c** are similar (Table 1), but phenyl-substituted **9d** gives potentials essentially identical with those of **9a** ($E°_1$ 0.25 vs 0.24 V; $E°_2$ 0.54 vs 0.52 V). The $E°$ values of the corresponding methyl complexes are also very close (**1d**/**1a**: 0.18 vs 0.19 V).[12] Thus, while tris(*p*-phenylphenyl)phosphine is certainly bulkier than triphenylphosphine, it should not be regarded as more electron releasing. The tricyclohexylphosphine complex **9e** is the easiest to oxidize, as was also observed for the corresponding methyl complexes.[12]

Scheme 4. Cross-Coupling to a ReC_6Re Complex



In experiments parallel to those with **4b** and $AgSbF_6$ in Scheme 2, **10b** and **9b**−**e** were treated with a variety of oxidizing agents. Numerous low-temperature NMR, IR, and ESR monitoring conditions were employed. In one representative series of experiments, ESR tubes were charged with **10b** or **9b**−**d** and cooled to −80 °C. Then saturated CH_2Cl_2 solutions of various ferrocenium salts were added. The tubes were immediately frozen in liquid nitrogen. ESR spectra were recorded from 10 K to ambient temperature. However, no type of signal—characteristic undecet, hextet, or otherwise—was observed. In NMR experiments directed at the low-temperature generation of dications, a multitude of resonances always formed. Other probes were similarly disappointing.

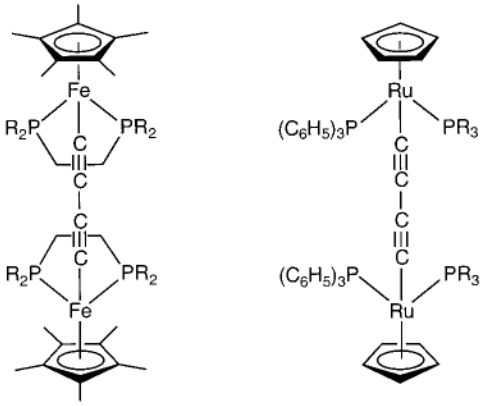
To obtain some qualitative stability data, cyclic voltammograms of **4a** and **9a**,**e** were recorded under special conditions. Potentials were applied only past the first oxidations (radical cation generation), followed by a delay before returning the potentials to the starting points. With **4a**, the ratio of the anodic and cathodic currents (i_a/i_c) decreased with increasing delays (0, 10, 30, 120, 300, 600 s: 1.00, 0.91, 0.87, 0.77, 0.76, 0.70). In other words, the return reductive scans gave larger "peaks", consistent with ongoing oxidation during the delays and high radical cation stability. With **9a**, the trend was opposite (0, 10, 30, 120, 300, 600 s: 1.07, 1.33, 1.37, 1.36, 1.56, 1.71), requiring a much less stable radical cation. However, **9e** behaved more like **4a** (0, 10, 30, 60, 300, 600 s: 1.05, 1.06, 1.08, 1.07, 0.91, 0.81), thereby showing the radical cation $\mathbf{9e}^{\bullet+}$ to be much more persistent than $\mathbf{9a}^{\bullet+}$.

Discussion

The preceding data show that the replacement of the triphenylphosphine in dirhenium μ-polyynediyl complexes $(\eta^5\text{-}C_5Me_5)Re(NO)(P(C_6H_5)_3)(C{\equiv}C)_n((C_6H_5)_3P)(ON)Re(\eta^5\text{-}C_5Me_5)$ by more electron rich para-substituted triarylphosphines (**b**,**c**) or tricyclohexylphosphine (**e**) dramatically facilitates oxidation and markedly improves the chemical reversibility of these oxidations. Chart 2 highlights similar results of Lapinte and Bruce with MC_4M systems. Replacement of the phosphorus-phenyl groups in the diiron μ-butadiynediyl complex **12a** by more electron releasing *i*-propyl groups (**12f**) renders oxidations 280 ($E_1°$) to 140 ($E_2°$, $E_3°$) mV more favorable.[3e] Replacement of two of the triphenylphosphine ligands of diruthenium complex **13a** by trimethylphosphine (**13g**) renders oxidations 30 ($E_1°$), 80 ($E_2°$), and 60 mV ($E_3°$) more favorable.[4a]

The cyclopentadienyl and phosphine ligands in FeC_4Fe complexes **12a**,**f** are electron releasing, with only modest π-accepting capabilities. In contrast, our rhenium complexes contain one strongly π-accepting ligand, nitrosyl. Thus, the ReC_4Re complexes **4a**,**b** would be expected to be less electron rich than **12a**,**f**. Accordingly, they are thermodynamically much more difficult to oxidize (≥460 mV, $E°_1$). Furthermore, **12a**,**f** undergo a third chemically reversible oxidation, giving systems of the type **D** (Scheme 1). The trication $\mathbf{12f}^{3+}(PF_6^-)_3$ could even be isolated and crystallographically characterized.[3e] The RuC_4Ru complexes **13a**,**g** also lack good π-accepting ligands, and cyclic voltammograms show four oxidations (three chemically reversible). Lapinte and Bruce have carefully analyzed the electronic ground states of their tri- and tetracations,[3e,4a] a theme beyond the scope of this paper.

Chart 2. Effect of Phosphine Ligand on Redox Potentials in Other MC_xM Complexes



12a,f **13a,g**

R = **a** C_6H_5
f *i*-C_3H_7

R = **a** C_6H_5
g CH_3

	$E°_1$	$E°_2$	$E°_3$	$E_{4p,a}$
12a[a]	−0.68	−0.04	+0.95	–
12f[a]	−0.97	−0.18	+0.81	–
13a[b]	−0.23	+0.41	+1.03	+1.68[c]
13g[b]	−0.26	+0.33	+0.97	+1.46[c]

a) Conditions: analogous to Table 1 and Figure 1 (reference 3e).

b) Conditions: CH_2Cl_2, 0.1 M *n*-$Bu_4N^+BF_4^-$, 25 °C, Pt working, counter and pseudo-reference electrodes (reference 4a). The corresponding values for **13a** under the conditions of **12a**,**f** are −0.20, +0.45, +1.07, and +1.68: C. Lapinte and M. Bruce, personal communication of work in progress.

c) Irreversible oxidations.

Table 1 shows that the effect of triarylphosphine **b** upon the redox potentials of the ReC_6Re and ReC_8Re complexes is less than with the ReC_4Re complexes (80−70 mV for **10b**/**10a** and **9b**/**9a** vs 230 mV for **4a**/**4b**). A possible rationale is that the HOMO has more rhenium character at shorter chain lengths, and the influence of the phosphine ligand more directly felt.[20] Nonetheless, all of these shifts are substantial. The slightly bulkier triarylphosphine **c** has a slightly diminished effect (60−40 mV for **9c**/**9a**). Consistent with the usual pattern for trialkyl- vs triarylphosphines, tricyclohexylphosphine gives the largest shifts (130−90 mV for **9e**/**9a**).

Despite the more favorable potentials, numerous low-temperature preparative experiments show that $\mathbf{10b}^{n+}(X^-)_n$ and $\mathbf{9b,c}^{n+}(X^-)_n$ (n = 1, 2) do not exhibit dramatically greater stabilities than the triphenylphosphine analogues. We find the negative results with $\mathbf{10b}^{n+}(X^-)_n$

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[20] This complex issue is currently being probed computationally: Jiao, H.; Gladysz, J. A. Manuscript in preparation.

particularly surprising, as this represents just a two-carbon extension of the very tractable systems **4a**,**b**$^{n+}$(X^-)$_n$. The tris(*p*-phenylphenyl)phosphine complex **9d**, which is not more readily oxidized than **9a** (Table 1) but offers a bulkier ligand environment, appears to represent another strategic dead end. Our more limited preparative data with tricyclohexylphosphine complex **9e** are similar, but the cyclic voltammograms with the delayed return sweep at least provide a "proof of concept"—i.e., with sufficient time resolution, bulkier and more electron rich phosphine ligands do measurably enhance the stabilities of radical cations **9**$^{\bullet+}\mathrm{X}^-$.

To date, the only preparatively successful oxidation of a MC$_x$M complex with more than four carbons has been reported by Lapinte.[3b] He was able to isolate the C$_8$ radical cation [(η^5-C$_5$Me$_5$)Fe(dppe)(C≡C)$_4$(dppe)Fe(η^5-C$_5$Me$_5$)]$^{\bullet+}$PF$_6^-$ in analytically pure form. Importantly, this proved to be a class III mixed-valence compound, with the odd electron fully delocalized between the iron end groups by all available criteria. This represents a particularly important property to characterize as a function of chain length and is a primary motivation of our ongoing efforts. Recently, "conjugal" iron/rhenium C$_x$ complexes (η^5-C$_5$Me$_5$)Fe(dppe)(C≡C)$_n$((C$_6$H$_5$)$_3$P)(ON)Re(η^5-C$_5$Me$_5$) have been reported (n = 2–4).[7,14] The heterobimetallic FeC$_4$Re system can be isolated in three oxidation states, and the redox chemistry of the higher homologues is under investigation. The spectroscopic properties of these compounds clearly show the iron end group to be more electron rich, consistent with the redox potential trends noted above.

The properties of the triphenylphosphine analogues **4b**$^{n+}$(SbF$_6^-$)$_n$, **10b**, and **9b**–**e** have been extensively analyzed in two previous full papers—including detailed comparisons with many compounds reported by others.[6,8] To minimize redundancy, the remaining discussion is cast within the framework of these triphenylphosphine analogues. First, any trends in the series **4b**/**10b**/**9b** represent chain length effects. For example, the IR ν_{NO} values (1622/1638/1643 cm^{-1}), Re*C*≡*C* ^{13}C NMR chemical shifts (C$_\alpha$ 96.6–95.7/104.9/110.7; C$_\beta$ 118.0/114.8–114.7/114.6), and UV–visible absorption patterns (Experimental Section) vary similarly to those of **4a**/**10a**/**9a**. We view the first as primarily an inductive effect, but, as analyzed earlier, other secondary factors must be in play.[8]

The absolute values of $E°_1$ and $E°_2$ (Table 1 and Figure 1) also show trends parallel to those of **4a**/**10a**/**9a**. The former is more strongly affected, and thus the difference between $E°_1$ and $E°_2$ diminishes. The complex underlying reasons have been previously discussed.[8] The most important consequence involves the comproportionation constant (K_c), which increases with the difference. This represents the equilibrium constant for reaction of the neutral and dicationic complexes to give the radical cation and usually tracks the resonance stabilization of class III mixed-valence species. The K_c values are summarized in Table 1, and that for **4b**$^{\bullet+}\mathrm{X}^-$ is very large, identical with that of the triphenylphosphine analogue (1.1 × 10^9). These decrease by several orders of magnitude for each step in the series **10a**,**b**$^{\bullet+}\mathrm{X}^-$ and **9a**,**b**$^{\bullet+}\mathrm{X}^-$. Under identical conditions, Lapinte's isolable FeC$_8$Fe radical cation gives a larger value than **9a**,**b**$^{\bullet+}\mathrm{X}^-$ (2.0 × 10^7 (20 °C) vs 5.9–8.8 × 10^4), analogous to the trend for the MC$_4$M complexes.[8]

In the C$_8$ series **9a**/**9b**/**9c**/**9d**/**9e**, the K_c values show a modest phosphine dependence. The equilibrium is most favorable for the most electron rich system, tricyclohexylphosphine complex **9e**$^{\bullet+}\mathrm{X}^-$ (2.8 × 10^5). Small phosphine dependences are also evident in the IR ν_{NO} values. Those of the methyl complexes **1a**–**e** vary over a narrow range (1606, 1603, 1601, 1606, 1599 cm^{-1}).[12] The C$_8$ complexes **9a**–**e** show a largely comparable pattern (1648, 1643, 1642, 1642, 1642 cm^{-1}), as well as **2a**–**c**,**e**$^+$BF$_4^-$ (1705, 1703, 1702, 1699 cm^{-1}), **3a**–**c**,**e** (1637, 1634, 1633, 1627 cm^{-1}), **4a**,**b** (1623, 1622 cm^{-1}), and **10a**,**b** (1640, 1638 cm^{-1}). The UV spectrum of **9d**, a compound that contains twice as many phenyl groups as **9a**–**c**, exhibits a much higher extinction coefficient for the second highest energy band. In contrast, **9e**, which lacks phenyl groups, gives less intense high energy bands.

The near-IR absorptions of mixed-valence compounds can be used to calculate electronic coupling parameters V_{ab}.[18] With class III compounds such as **4b**$^{\bullet+}$SbF$_6^-$, this can be regarded as a resonance stabilization energy. Although this subject is complicated by many subtle issues of interpretation,[21] V_{ab} represents the best parameter for comparing different compounds. However, **4b**$^{\bullet+}$SbF$_6^-$ gives (like the triphenylphosphine analogue **4a**$^{\bullet+}$PF$_6^-$) three near-IR bands (Figure 4), whereas most mixed-valence complexes give only one. One rationale considered earlier[6] is spin–orbit coupling, which is more pronounced in third-row transition metals and can lift degeneracies associated with optical transitions. For example, class III[22,23] and class II[23] diosmium complexes exhibit multiple near-IR bands. However, alternative interpretations may gain support as further data are collected on related compounds.[24] Some trends suggest that one absorption might be a LMCT transition, and another a MLCT transition.

Regardless, standard protocols do not yet exist for calculating V_{ab} values of mixed-valence compounds that exhibit multiple spin–orbit-derived near-IR absorptions. In view of this and the other ambiguities in assignments, Table 2 presents data derived from all three bands. The range (5600, 4900, 4100 cm^{-1}) is actually not very large, and the individual values are essentially identical with those of **4a**$^{\bullet+}$PF$_6^-$ (5600, 5000, 4200 cm^{-1}).[6] These represent, together with quantities derived from the diiron and diruthenium MC$_4$M systems in Chart 2, some of the highest values in the literature. Together, these results reflect the impressive ability of the wire-like C$_4$ bridge to delocalize charge between two metal termini.

Other quantities can be useful in comparing mixed-valence compounds. For example, a common test for class III complexes is to calculate the bandwidths $\Delta\tilde{\nu}_{1/2}$

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[21] Nelsen, S. F. *Chem. Eur. J.* **2000**, *6*, 581.

[22] (a) Richardson, D. E.; Sen, J. P.; Buhr, J. D.; Taube, H. *Inorg. Chem.* **1982**, *21*, 3136. (b) Hornung, F. M.; Baumann, F.; Kaim, W.; Olabe, J. A.; Slep, L. D.; Fiedler, J. *Inorg. Chem.* **1998**, *37*, 311.

[23] (a) Demadis, K. D.; Neyhart, G. A.; Kober, E. M.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 5948. (b) Demadis, K. D.; El-Samanody, E.-S.; Coia, G. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 535.

[24] For some class III mixed-valence diiron complexes that give several near-IR bands, see: Le Stang, S.; Paul, F.; Lapinte, C. *Organometallics* **2000**, *19*, 1035 (spin–orbit coupling is much weaker for first-row transition metals).

according to the formula for class II systems. These values are given in the last column (5090−4340 cm^{-1}) and are 3 times greater than those observed (1500−1200 cm^{-1}). Hence, in accord with the IR and ESR conclusions, $\mathbf{4b}^{\bullet+}SbF_6^-$ fails what is often regarded as a diagnostic criterion for class II complexes. The V_{ab} values associated with this class II formula are also included, as a reference point to other literature treatments.

In summary, this paper has described our "second generation" approach to longer chain homologues of the ReC_4Re radical cation $\mathbf{4a}^{\bullet+}X^-$ and dication $\mathbf{4a}^{2+}(X^-)_2$. Although good evidence for enhanced stabilities was obtained, the key issue proved not to be one of isolability but of detectability. It is probable that other types of probes (e.g., spectroelectrochemistry) might allow some degree of in situ characterization. However, we sought breakthroughs into new stability regimes as opposed to incremental improvements. We note in passing that our work with the methyl complex radical cations $\mathbf{1b}\text{-}\mathbf{e}^{\bullet+}X^-$ also established a marked anion effect—enhanced stabilities associated with the "BAr_F^-" anion $B(3,5\text{-}C_6H_3\text{-}(CF_3)_2)_4^-$—an additional tactic not employed above. Nonetheless, we have abandoned these end groups for more promising third-generation rhenium Lewis acids. Regardless, the above data provide an instructive example of design and tactics in targeted organometallic synthesis, and successful strategies will be described in due course.[25]

Experimental Section[26]

$[(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4CH_3)_3)(HC{\equiv}CH)]^+BF_4^-$ ($\mathbf{2b}^+BF_4^-$). A Schlenk flask was charged with $(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4CH_3)_3)(CH_3)$ (**1b**;[12] 0.470 g, 0.700 mmol) and chlorobenzene (15 mL) and cooled to −45 °C (CH_3CN/CO_2). Then $HBF_4{\cdot}OEt_2$ (0.13 mL, 0.77 mmol) was added with stirring. After 10 min, acetylene was bubbled through the mixture. After 10 min, the flask was transferred into a silicone oil bath and heated to 80 °C. After 30 min, the acetylene stream was halted and the bath removed. The solvent was removed by oil pump vacuum. The residue was dissolved in a minimum of CH_2Cl_2. The sample was filtered into rapidly stirred Et_2O (500 mL). The cream-colored precipitate was collected by filtration, washed with Et_2O, and air-dried to give $\mathbf{2b}^+BF_4^-$ (0.401 g, 0.522 mmol, 75%): mp 215−216 °C dec. Anal. Calcd for $C_{33}H_{38}NOPReBF_4$: C, 51.57; H, 4.98. Found: C, 51.68; H, 5.00. IR:[28] ν_{NO} 1703 vs. MS:[29] 682 ($\mathbf{2b}^+$, 100%).

NMR (CD_2Cl_2):[30] ^1H 7.79 (d, J_{HP} = 4.8, $HC{\equiv}$ anti to PR_3),[31] 7.44−7.31 (m, part of $3C_6H_4$), 7.25−6.99 (m, part of $3C_6H_4$), 6.93 (d, J_{HP} = 18.8, $HC{\equiv}$ syn to PR_3),[31] 2.46 (s, $3ArCH_3$), 1.78 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ 144.2−143.1 (m, C_6H_4), 134.3−133.3 (m, C_6H_4), 130.4 (s, C_6H_4), 108.8 (s, $C_5(CH_3)_5$), 100.6 (s, $HC{\equiv}$ anti to PR_3),[31] 92.2 (d, J_{CP} = 15.6, $HC{\equiv}$ syn to PR_3),[31] 28.2 (s, $ArCH_3$), 9.8 (s, $C_5(CH_3)_5$); $^{31}P\{^1H\}$ 16.3 (s).

$(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4CH_3)_3)(C{\equiv}CH)$ (3b). A Schlenk flask was charged with $\mathbf{2b}^+BF_4^-$ (0.385 g, 0.501 mmol) and *t*-BuOK (0.069 g, 0.61 mmol) and cooled to −80 °C (2-propanol/CO_2). Then THF (10 mL) was added with stirring. After 20 min, the cooling bath was removed. After an additional 2 h, solvent was removed by oil pump vacuum, and benzene (3 mL) was added. The extract was filtered through Celite (4 cm). Solvent was removed from the filtrate by oil pump vacuum. The residue was dissolved in CH_2Cl_2 (1 mL), and hexane (5 mL) was added. The solvent was removed by rotary evaporation. The residue was dried by oil pump vacuum to give **3b** as an orange powder (0.325 g, 0.471 mmol, 95%): mp 197−198 °C.[32] Anal. Calcd for $C_{33}H_{37}NOPRe$: C, 58.22; H, 5.48. Found: C, 58.29; H, 5.62. IR:[28] $\nu_{C\equiv C}$ 1937 m, ν_{NO} 1634 vs. MS:[29] 681 ($\mathbf{3b}^+$, 100%).

NMR (C_6D_6):[30] ^1H 7.81 (dd, J_{HP} = 10.8, J_{HH} = 8.2, 3*o*-C_6H_4), 6.95 (dd, J_{HP} = 1.7, J_{HH} = 8.3, 3*m*-C_6H_4), 3.32 (d, J_{HP} = 2.6, ${\equiv}CH$), 1.99 (s, $3ArCH_3$), 1.73 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ 139.8 (s, *p*-C_6H_4), 134.7 (d, J_{CP} = 10.8, *o*-C_6H_4), 133.3 (d, J_{CP} = 52.9, *i*-C_6H_4), 128.9 (d, J_{CP} = 9.7, *m*-C_6H_4), 111.5 (s, $C{\equiv}CH$), 99.7 (s, $C_5(CH_3)_5$), 98.5 (d, J_{CP} = 15.1, $ReC{\equiv}C$), 21.2 (s, $ArCH_3$), 10.3 (s, $C_5(CH_3)_5$); $^{31}P\{^1H\}$ 18.6 (s).

$(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4CH_3)_3)(C{\equiv}CC{\equiv}C)((4\text{-}H_3CC_6H_4)_3P)(ON)Re(\eta^5\text{-}C_5Me_5)$ (4b). A Schlenk tube was charged with **3b** (0.200 g, 0.294 mmol), $Cu(OAc)_2$ (0.079 g, 0.44 mmol), and pyridine (5 mL). The mixture was stirred at 80 °C for 2 h. The solvent was removed by oil pump vacuum. The residue was dissolved in THF (2 × 3 mL). Column chromatography (SiO_2, 8 cm, THF) gave an orange band. The solvent was removed by oil pump vacuum to give **4b** as an orange powder (0.140 g, 0.103 mmol, 70%; 58:42 diastereomer mixture), mp 159−162 °C dec. Anal. Calcd for $C_{66}H_{72}N_2O_2P_2Re_2$: C, 58.30; H, 5.34. Found: C, 58.87; H, 5.61. IR:[28] $\nu_{C\equiv C}$ 1963 w, ν_{NO} 1622 vs. UV−vis[33] (8.5×10^{-6} M) 232 (63 900), 270 sh (22 300), 352 (13 500). MS:[29] 1360 ($\mathbf{4b}^+$, 100%).

NMR (C_6D_6):[30] ^1H 7.87 (br d, J = 6.6, 6*o*-C_6H_4), 6.95 (dd, J = 11.8, 7.9, 6*m*-C_6H_4), 2.03, 2.00 (2 s, 58:42, $6ArCH_3$), 1.71 (br s, $2C_5(CH_3)_5$); $^{13}C\{^1H\}$ 139.9 (s, *p*-C_6H_4), 135.2 (s, *o*-C_6H_4), 134.6 (d, J_{CP} = 47.7, *i*-C_6H_4), 129.3 (s, *m*-C_6H_4), 118.0 (br s, $ReC{\equiv}C$), 100.5 (s, $C_5(CH_3)_5$), 96.6, 95.7 (2 br s, $ReC{\equiv}C$), 21.6 (s, $ArCH_3$), 10.5 (s, $C_5(CH_3)_5$); $^{31}P\{^1H\}$ 18.3 (br s).

$[(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4CH_3)_3)(C{\equiv}CC{\equiv}C)((4\text{-}H_3CC_6H_4)_3P)(ON)Re(\eta^5\text{-}C_5Me_5)]^{\bullet+}SbF_6^-$ ($\mathbf{4b}^{\bullet+}SbF_6^-$). A Schlenk tube was charged with **4b** (0.204 g, 0.150 mmol) and toluene (3 mL). A solution of $AgSbF_6$ (0.051 g, 0.19 mmol) in toluene (2 mL) was added dropwise with stirring. A dark green solid formed immediately and after 15 min was collected on a medium frit, washed with toluene (2 × 1 mL), and extracted with CH_2Cl_2 (5 mL). The extract was filtered through a Celite pad. The solvent was removed by oil pump vacuum. The residue was dissolved in a minimum of CH_3CN, and toluene (5 mL) was added. The solution was concentrated. The dark green powder was collected on a medium frit, washed with Et_2O, and dried by oil pump vacuum to give $\mathbf{4b}^{\bullet+}SbF_6^-$ (0.162 g, 0.104 mmol, 70%), mp 210−212 °C dec. Anal. Calcd for $C_{66}H_{72}F_6N_2O_2P_2Re_2Sb$: C, 49.69; H, 4.55. Calcd for $C_{66}H_{72}F_6N_2O_2P_2Re_2Sb{\cdot}2CH_2Cl_2$: C, 46.27; H, 4.34. Found: C, 46.05−46.21; H, 4.30−4.36. IR:[28] $\nu_{C\equiv C}$ 1873 m, ν_{NO} 1665 vs; UV−vis/near-IR:[33] (6.0×10^{-6} M) 232 (63 000), 354 (27 000), 452 (5800), 891 (24 000), 1020 (14 000), 1217 (5400). MS:[29] 1361 ($\mathbf{4b}^+$, 68%), 656 ($((C_5Me_5)Re(NO)(P(C_6H_4CH_3)_3)^+$, 100%); no other peaks above 350 of >19%.

$[(\eta^5\text{-}C_5Me_5)Re(NO)(P(4\text{-}C_6H_4CH_3)_3)(C{=}C{=}C{=}C)((4\text{-}H_3CC_6H_4)_3P)(ON)Re(\eta^5\text{-}C_5Me_5)]^{2+}(SbF_6^-)_2$ ($\mathbf{4b}^{2+}(SbF_6^-)_2$). A

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(25) Le Bras, J.; Meyer, W. E.; Gladysz, J. A. Unpublished results.

(26) General procedures, solvent purifications, and instrumentation were identical with those in five recent full papers[6,8,12,13,27] and are further detailed elsewhere.[14] Chlorobenzene was distilled from P_2O_5. Pyridine was distilled from KOH or NaOH.

(27) Dembinski, R.; Lis, T.; Szafert, S.; Mayne, C. L.; Bartik, T.; Gladysz, J. A. *J. Organomet. Chem.* **1999**, *578*, 229.

(28) In units of cm^{-1}, solvent CH_2Cl_2.

(29) Positive FAB (*m/z*), 3-NBA/CH_2Cl_2 or benzene unless noted (**8c**,**d**, 2-nitrophenyloctyl ether/benzene).

(30) All ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 300, 75.5, and 121 MHz, respectively. Chemical shifts and J values are given in δ and Hz, respectively. In disubstituted aryl rings, the designations ipso/ortho/meta/para are with respect to the phosphorus substituent.

(31) These assignments follow from coupling constant and chemical shift patterns rigorously established earlier.[16] For the syn/anti sense, see **II** in Chart 1.

(32) In other preparations, the CH_2Cl_2/hexane solution was kept at −20 °C for 14 h. Orange needles of **3b** were obtained (ca. 90%).

(33) In units of nm (ϵ, M^{-1} cm^{-1}), solvent CH_2Cl_2.

Schlenk tube was charged with $\mathrm{AgSbF_6}$ (0.080 g, 0.232 mmol) and toluene (5 mL). A solution of **4b** (0.110 g, 0.0809 mmol, 58:42 diastereomer mixture) in toluene (5 mL) was added dropwise with stirring. A deep blue solid formed immediately, which after 15 min was collected on a medium frit, washed with toluene (2 × 3 mL) and $\mathrm{Et_2O}$ (3 × 2 mL), air-dried, and extracted with $\mathrm{CH_2Cl_2}$ (5 mL). The extract was filtered through a Celite pad and concentrated to ca. 2 mL. Then $\mathrm{Et_2O}$ (7 mL) was added. The precipitate was isolated by filtration and dissolved in a minimum of $\mathrm{CH_3CN}$. Toluene (8 mL) was added. The dark blue microcrystals were isolated by filtration and dried by oil pump vacuum to give $\mathbf{4b}^{2+}(\mathrm{SbF_6}^-)_2$ (0.111 g, 0.0606 mmol, 75%; 53:47 diastereomer mixture), mp 241−243 °C dec. Anal. Calcd for $\mathrm{C_{66}H_{72}F_{12}N_2O_2P_2Re_2Sb_2}$: C, 43.24; H, 3.96. Calcd for $\mathrm{C_{66}H_{72}F_{12}N_2O_2P_2Re_2Sb_2{\cdot}CH_2Cl_2}$: C, 42.00; H, 3.89. Found: C, 41.82−41.86; H, 3.86−3.91. IR:[28] ν_{NO} 1719 vs. MS:[29] 1361 ($\mathbf{4b}^+$, 68%), 656 ($((\mathrm{C_5Me_5})\mathrm{Re(NO)(P(C_6H_4CH_3)_3)}^+$, 100%).

NMR ($\mathrm{CD_2Cl_2}$):[30] $^1\mathrm{H}$ 7.39−7.15 (m, $6\mathrm{C_6H_4}$), 2.42 (s, $6\mathrm{ArCH_3}$), 2.00, 1.95 (2 s, 46:54, $2\mathrm{C_5(CH_3)_5}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ (for one isomer, ReCC signals not observed) 144.5 (s, p-$\mathrm{C_6H_4}$), 133.5 (d, $J_{\mathrm{CP}} = 11.5$, o-$\mathrm{C_6H_4}$), 130.8 (d, $J_{\mathrm{CP}} = 12.3$, m-$\mathrm{C_6H_4}$), 125.6 (d, $J_{\mathrm{CP}} = 64.5$, i-$\mathrm{C_6H_4}$), 114.1 (s, $C_5\mathrm{(CH_3)_5}$), 21.8 (s, $\mathrm{ArCH_3}$), 10.6 (s, $\mathrm{C_5(}C\mathrm{H_3)_5}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ 24.1, 22.5 (2 s, 47:53).

$[(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Re(NO)(P(4\text{-}C_6H_4CH_3)_3)(HC{\equiv}CC{\equiv}CSiMe_3)}]^+\mathrm{BF_4}^-$ ($\mathbf{6b}^+\mathrm{BF_4}^-$). A Schlenk flask was charged with **1b** (0.572 g, 0.853 mmol) and chlorobenzene (ca. 40 mL) and cooled to −45 °C. Then $\mathrm{HBF_4{\cdot}OEt_2}$ (0.160 mL, 0.941 mmol) was added with stirring. After 10 min, $\mathrm{HC{\equiv}CC{\equiv}CSiMe_3}$ (0.269 g, 2.37 mmol) was added. The bath was warmed to room temperature. After 24 h, the solvent was removed by oil pump vacuum, and $\mathrm{CH_2Cl_2}$ (ca. 4 mL) was added. The solution was slowly added to rapidly stirring hexane. A light tan powder was collected by filtration and air-dried to give $\mathbf{6b}^+\mathrm{BF_4}^-$ (0.685 g, 0.792 mmol, 92%), mp 86−87 °C dec. Anal. Calcd for $\mathrm{C_{38}H_{46}BF_4NOPReSi}$: C, 52.77; H, 5.36. Found: C, 52.51; H, 5.45. IR:[28] $\nu_{\mathrm{C{\equiv}C}}$ 2139 w, ν_{NO} 1703 vs. MS:[29] 778 ($\mathbf{6b}^+$, 100%).

NMR ($\mathrm{CD_2Cl_2}$, major/minor rotamer):[30] $^1\mathrm{H}$ 7.06/8.20 (2 d, $J_{\mathrm{HP}} = 19/4.5$, $\mathrm{{\equiv}CH}$ syn/anti to $\mathrm{PR_3}$),[34] 7.44−6.86 (m, $3\mathrm{C_6H_4}$), 2.47/2.34 (2 s, $3\mathrm{ArCH_3}$), 1.84/1.76 (2 s, $\mathrm{C_5(CH_3)_5}$), 0.33/−0.36 (2 s, $\mathrm{Si(CH_3)_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ 144.7−144.1/143.6−143.1 (2 m, p-$\mathrm{C_6H_4}$), 134.1/133.0 (2 d, $J_{\mathrm{CP}} = 10$, o-$\mathrm{C_6H_4}$), 130.6/130.0 (d, $J_{\mathrm{CP}} = 8.7/11$, m-$\mathrm{C_6H_4}$), 130.1/− (d, $J_{\mathrm{CP}} = 51$, i-$\mathrm{C_6H_4}$), 114.9/113.2 (2 s, $C\mathrm{{\equiv}CSi}$), 110.4/110.1 (2 s, $C_5\mathrm{(CH_3)_5}$), 97.7/93.3 (2 d, $J_{\mathrm{CP}} = 18/7.3$, $\mathrm{H}C\mathrm{{\equiv}C}$ syn/anti to $\mathrm{PR_3}$),[34] 95.3/108.5 (2 s, $\mathrm{C{\equiv}}C\mathrm{Si}$), 92.5/86.6 (2 d, $J_{\mathrm{CP}} = 3.7/12$, $\mathrm{HC{\equiv}}C$ anti/syn to $\mathrm{PR_3}$),[34] 21.8/21.6 (2 s, $\mathrm{ArCH_3}$), 9.9/9.9 (s, $\mathrm{C_5(}C\mathrm{H_3)_5}$), −0.3/−0.9 (2 s, $\mathrm{Si(CH_3)_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ 19.0/14.8 (2 s, 22:78).

$(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Re(NO)(P(4\text{-}C_6H_4CH_3)_3)(C{\equiv}CC{\equiv}CSiMe_3)}$ (7b). A Schlenk flask was charged with $\mathbf{6b}^+\mathrm{BF_4}^-$ (0.566 g, 0.654 mmol) and THF (ca. 50 mL), and cooled to −80 °C. Then t-BuOK (1 M in THF; 0.78 mL, 0.78 mmol) was added with stirring. After 10 min, the cold bath was removed. After 2 h, the solvent was removed by oil pump vacuum, and benzene (5 mL) was added. The mixture was filtered through a Celite pad (1−2 cm). The solvent was removed by oil pump vacuum. The dark red oil was dissolved in $\mathrm{CH_2Cl_2}$ (ca. 2 mL), and hexane (ca. 20 mL) was added. The solvent was removed by rotary evaporation and oil pump vacuum to give **7b** as an orange powder (0.447 g, 0.575 mmol, 88%), mp 113−123 °C dec. Anal. Calcd for $\mathrm{C_{38}H_{45}NOPReSi}$: C, 58.74; H, 5.84. Found: C, 59.20; H, 6.16. IR:[28] $\nu_{\mathrm{C{\equiv}C}}$ 2114 m, 2094 s, ν_{NO} 1645 vs. MS (m/z, EI, $\mathrm{CH_2Cl_2}$): 777 ($\mathbf{7b}^+$, 100%); no other peaks above 400 of >5%.

NMR ($\mathrm{C_6D_6}$):[30] $^1\mathrm{H}$ 7.69 (dd, $J_{\mathrm{HP}} = 11.0$, $J_{\mathrm{HH}} = 8.0$, $3o$-$\mathrm{C_6H_4}$), 6.87 (br d, $J_{\mathrm{HH}} = 7.0$, $3m$-$\mathrm{C_6H_4}$), 1.97 (s, $3\mathrm{ArCH_3}$), 1.61 (s, $\mathrm{C_5(CH_3)_5}$), 0.18 (s, $\mathrm{Si(CH_3)_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ 140.5 (d, $J_{\mathrm{CP}} = 2.1$, p-$\mathrm{C_6H_4}$), 134.7 (d, $J_{\mathrm{CP}} = 10.9$, o-$\mathrm{C_6H_4}$), 132.9 (d, $J_{\mathrm{CP}} = 53.2$, i-$\mathrm{C_6H_4}$), 129.5 (d, $J_{\mathrm{CP}} = 10.6$, m-$\mathrm{C_6H_4}$), 112.8 (s, $\mathrm{ReC{\equiv}}C$),[34] 107.0 (d, $J_{\mathrm{CP}} = 15.8$, $\mathrm{Re}C\mathrm{{\equiv}C}$),[34] 100.8 (s, $C_5\mathrm{(CH_3)_5}$), 94.1 (d, $J_{\mathrm{CP}} = 2.4$, $C\mathrm{{\equiv}C{-}Si}$),[34] 80.7 (s, $\mathrm{C{\equiv}}C\mathrm{Si}$),[34] 21.5 (s, $\mathrm{ArCH_3}$), 10.4 (s, $\mathrm{C_5(}C\mathrm{H_3)_5}$), 1.2 (s, $\mathrm{Si(CH_3)_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ 18.3 (s).

$(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Re(NO)(P(4\text{-}C_6H_4CH_3)_3)(C{\equiv}CC{\equiv}CH)}$ (8b). A Schlenk flask was charged with **7b** (0.159 g, 0.204 mmol), $\mathrm{K_2CO_3}$ (0.026 g, 0.19 mmol), and methanol (ca. 20 mL). The mixture was stirred for 24 h. The solvent was removed by rotary evaporation, and benzene (3 mL) was added. The mixture was filtered through Celite (1−2 cm). The solvent was removed by rotary evaporation. The orange oil was dissolved in $\mathrm{CH_2Cl_2}$ (ca. 1 mL), and hexane (ca. 20 mL) was added. The solvent was removed by rotary evaporation to give crude **8b** as an orange powder (0.117 g, 0.160 mmol, (93−95):(7−5) **8b**/**7b**, ca. 76%), mp 164−180 °C dec (no melting; orange/brown/black color transition).[19] A sample was washed with hexane for microanalysis. Anal. Calcd for $\mathrm{C_{35}H_{37}NOPRe}$: C, 59.64; H, 5.29. Found: C, 59.39; H, 5.33. IR:[28] $\nu_{\mathrm{C{\equiv}C}}$ 2113 s, 1975 w, ν_{NO} 1643 vs. MS:[29] 705 ($\mathbf{8b}^+$, 27%), 777 ($\mathbf{7b}^+$, 100%), 656 ($((\mathrm{C_5Me_5})\mathrm{Re(NO)(P(C_6H_4CH_3)_3)}^+$, 57%); no other peaks above 400 of >5%.

NMR ($\mathrm{C_6D_6}$):[30] $^1\mathrm{H}$ 7.73 (dd, $J_{\mathrm{HP}} = 11.0$, $J_{\mathrm{HH}} = 8.0$, $3o$-$\mathrm{C_6H_4}$), 6.90 (dd, $J_{\mathrm{HP}} = 1.7$, $J_{\mathrm{HH}} = 8.0$, $3m$-$\mathrm{C_6H_4}$), 2.00 (d, $J_{\mathrm{HP}} = 1.2$, $\mathrm{{\equiv}CH}$), 1.97 (s, $3\mathrm{ArCH_3}$), 1.63 (s, $\mathrm{C_5(CH_3)_5}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ 140.5 (d, $J_{\mathrm{CP}} = 2.2$, p-$\mathrm{C_6H_4}$), 134.8 (d, $J_{\mathrm{CP}} = 11.1$, o-$\mathrm{C_6H_4}$), 133.0 (d, $J_{\mathrm{CP}} = 53.5$, i-$\mathrm{C_6H_4}$), 129.5 (d, $J_{\mathrm{CP}} = 10.6$, m-$\mathrm{C_6H_4}$), 111.4 (s, $\mathrm{ReC{\equiv}}C$),[34] 103.0 (d, $J_{\mathrm{CP}} = 16.2$, $\mathrm{Re}C\mathrm{{\equiv}C}$),[34] 100.7 (s, $C_5\mathrm{(CH_3)_5}$), 73.0 (d, $J_{\mathrm{CP}} = 2.9$, $C\mathrm{{\equiv}CH}$),[34] 65.5 (s, $\mathrm{C{\equiv}}C\mathrm{H}$),[34] 21.5 (s, $\mathrm{ArCH_3}$), 10.4 (s, $\mathrm{C_5(}C\mathrm{H_3)_5}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ 18.3 (s).

$(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Re(NO)(P(4\text{-}C_6H_4CH_3)_3)(C{\equiv}C)_4((4\text{-}H_3CC_6H_4)_3P)(ON)Re}(\eta^5\text{-}\mathrm{C_5Me_5})$ (9b). A Schlenk flask was charged with **8b** (0.052 g, 0.074 mmol), $\mathrm{Cu(OAc)_2}$ (0.014 g, 0.078 mmol), and pyridine (ca. 3 mL). The mixture was stirred for 1 h at 50 °C. The solvent was removed by oil pump vacuum, and benzene (5 mL) was added. The mixture was filtered through Celite (1−2 cm). The solvent was removed by rotary evaporation. The sample was passed through silica (7−8 cm, THF/hexane, 1:3 → 1:2). The solvent was removed by rotary evaporation. The oil was dissolved in $\mathrm{CH_2Cl_2}$ (2 mL), and hexane (10 mL) was added. The solvent was removed by rotary evaporation and oil pump vacuum to give **9b** as an orange powder (0.020 g, 0.014 mmol, 38%; 50:50 diastereomer mixture), mp 202−221 °C dec. Anal. Calcd for $\mathrm{C_{70}H_{72}N_2O_2P_2Re_2}$: C, 59.73; H, 5.16. Found: C, 59.86; H 5.24. IR:[28] $\nu_{\mathrm{C{\equiv}C}}$ 2107 s, 1954 m, ν_{NO} 1643 vs. UV−vis[33] (7.67×10^{-6} M) 234 (83 000), 362 (75 000), 394 (71 000). MS:[29] 1408 ($\mathbf{9b}^+$, 100%), 656 ($((\mathrm{C_5Me_5})\mathrm{Re(NO)(P(C_6H_4CH_3)_3)}^+$, 66%); no other peaks above 400 of >11%.

NMR ($\mathrm{CD_2Cl_2}$):[30] $^1\mathrm{H}$ 7.72 (dd, $J_{\mathrm{HP}} = 10.5$, $J_{\mathrm{HH}} = 8.0$, $3o$-$\mathrm{C_6H_4}$), 6.88 (br d, $J_{\mathrm{HH}} = 7.0$, $3m$-$\mathrm{C_6H_4}$), 1.98 (s, $3\mathrm{ArCH_3}$), 1.60 (s, $\mathrm{C_5(CH_3)_5}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ 140.5 (d, $J_{\mathrm{CP}} = 3.1$, p-$\mathrm{C_6H_4}$), 134.7 (d, $J_{\mathrm{CP}} = 10.8$, o-$\mathrm{C_6H_4}$), 132.8 (d, $J_{\mathrm{CP}} = 54$, i-$\mathrm{C_6H_4}$), 129.5 (d, $J_{\mathrm{CP}} = 10.8$, m-$\mathrm{C_6H_4}$), 114.6 (s, $\mathrm{ReC{\equiv}}C$), 110.7 (d, $J_{\mathrm{CP}} = 12.7$, $\mathrm{Re}C\mathrm{{\equiv}C}$), 101.0 (s, $C_5\mathrm{(CH_3)_5}$), 67.9 (s, $\mathrm{ReC{\equiv}C}C$), 66.0 (s, $\mathrm{ReC{\equiv}CC{\equiv}}C$), 21.6 (s, $\mathrm{ArCH_3}$), 10.4 (s, $\mathrm{C_5(}C\mathrm{H_3)_5}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ 17.9, 17.8 (2 s, 50:50).

$(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Re(NO)(P(4\text{-}C_6H_4CH_3)_3)(C{\equiv}C)_3((4\text{-}H_3CC_6H_4)_3P)(ON)Re}(\eta^5\text{-}\mathrm{C_5Me_5})$ (10b). One Schlenk flask was charged with **8b** (0.2931 g, 0.4158 mmol) and toluene (5 mL). Another was charged with **3b** (0.2852 g, 0.4189 mmol), $\mathrm{Cu(OAc)_2}$ (0.181 g, 0.996 mmol), and pyridine (5 mL) and placed in a 60 °C oil bath. Over 5 min, the solution of **8b** was added to the solution of **3b** via syringe. The mixture was kept at 70 °C for 20 min. The solvent was removed by oil pump vacuum. The dark residue was extracted with a minimum of THF. The extract was filtered through silica (3−4 cm). The solvent was removed by rotary evaporation. Column chromatography ($\mathrm{SiO_2}$, 23 cm, THF/hexanes, 1:3) yielded two fractions, from which solvents were removed by oil pump vacuum. The first gave **10b** as an orange powder (0.130 g, 0.0939 mmol, 23%; 50:50 diastereomer mixture that enriched upon reprecipitation or attempted crystallization), mp 202−205 °C dec (the second gave **9b** (0.018 g, 0.013 mmol, 3%); no **4b** was detected. Anal.

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[34] These assignments follow from coupling constant and chemical shift patterns rigorously established earlier.[17]

Calcd for $C_{68}H_{72}N_2O_2P_2Re_2$: C, 59.03; H, 5.24. Found: C, 58.92; H, 5.55. IR:[28] $\nu_{C\equiv C}$ 2059 w, ν_{NO} 1638 vs. UV−vis[33] (8.67 × 10^{-6} M) 232 (82 000), 320 (38 200), 358 (37 800). MS:[29] 1384 (**10b**$^+$, 100%).

NMR (C_6D_6):[30] ^1H 7.77 (dd, J_{HP} = 10.7, J_{HH} = 8.0, 3*o*-C_6H_4), 6.86 (br d, J_{HH} = 8.0, 3*m*-C_6H_4), 1.99 (s, 3ArCH$_3$), 1.64 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ 140.2 (d, J_{CP} = 2.1, *p*-C_6H_4), 134.8 (d, J_{CP} = 10.9, *o*-C_6H_4), 133.3 (d, J_{CP} = 53.6, *i*-C_6H_4), 129.4 (d, J_{CP} = 10.3, *m*-C_6H_4), 114.8, 114.7 (2 s, ReC≡*C*), 104.9 (d, J_{CP} = 16.6, Re*C*≡C), 100.8 (s, *C*$_5$(CH$_3$)$_5$), 66.6 (br s, ReC≡C*C*), 21.6 (s, ArCH$_3$), 10.5 (s, C$_5$(*C*H$_3$)$_5$); $^{31}P\{^1H\}$ 18.4, 18.3 (2 s, 65:35).

[(η^5-C$_5$Me$_5$)Re(NO)(P(4-C$_6$H$_4$-*t*-C$_4$H$_9$)$_3$)(HC≡CH)]$^+$BF$_4^-$ (2c$^+$BF$_4^-$). The complex (η^5-C$_5$Me$_5$)Re(NO)(P(4-C$_6$H$_4$-*t*-C$_4$H$_9$)$_3$)(CH$_3$) (**1c**;[12] 0.976 g, 1.22 mmol), chlorobenzene (20 mL), HBF$_4$·OEt$_2$ (0.22 mL, 1.3 mmol), and acetylene were combined in a procedure analogous to that for **2b**$^+$BF$_4^-$. An identical workup gave **2c**$^+$BF$_4^-$ as a cream precipitate (0.881 g, 0.985 mmol, 80%), mp 165−166 °C dec. Anal. Calcd for $C_{42}H_{56}BF_4NOPRe$: C, 56.37; H, 6.31. Found: C, 55.01; H, 6.16. IR:[28] ν_{NO} 1702 vs. MS:[29] 808 (**2c**$^+$, 100%).[35]

NMR (CD$_2$Cl$_2$):[30] ^1H 7.86 (d, J_{HP} = 4.7, HC≡ anti to PR$_3$),[31] 7.64−7.10 (m, 3C$_6$H$_4$), 7.03 (d, J_{HP} = 18.7, HC≡ syn to PR$_3$),[31] 1.76 (s, C$_5$(CH$_3$)$_5$), 1.37, 1.28 (2 br s, 3ArC(CH$_3$)$_3$); $^{13}C\{^1H\}$ 157.0−155.0 (m, C$_6$H$_4$), 135.0−133.0 (m, C$_6$H$_4$), 127.2−126.4 (m, C$_6$H$_4$), 109.0 (s, *C*$_5$(CH$_3$)$_5$), 100.9 (s, HC≡ anti to PR$_3$),[31] 92.2 (d, J_{CP} = 16.3, HC≡ syn to PR$_3$),[31] 35.5 (s, Ar*C*(CH$_3$)$_3$), 31.3 (s, ArC(*C*H$_3$)$_3$), 9.8 (s, C$_5$(*C*H$_3$)$_5$); $^{31}P\{^1H\}$ 15.9 (s).

(η^5-C$_5$Me$_5$)Re(NO)(P(4-C$_6$H$_4$-*t*-C$_4$H$_9$)$_3$)(C≡CH) (3c). The complex **2c**$^+$BF$_4^-$ (0.100 g, 0.112 mmol), THF (8 mL), and *t*-BuOK (1.0 M in THF; 0.125 mL, 0.125 mmol) were combined in a procedure analogous to that for **3b**. An identical workup gave **3c** as an orange powder (0.060 g, 0.075 mmol, 67%), mp 221−223 °C dec. Anal. Calcd for $C_{42}H_{55}NOPRe$: C, 62.50; H, 6.87. Found: C, 62.35; H, 6.99. IR:[28] $\nu_{C\equiv C}$ 1936 w, ν_{NO} 1633 vs. MS:[29] 807 (**3c**$^+$, 19%), 782 ((C$_5$Me$_5$)Re(NO)(P(C$_6$H$_4$C$_4$H$_9$)$_3$)$^+$, 56%), 916 (100%); no other peaks above 450 of >8%.[35]

NMR (CD$_2$Cl$_2$):[30] ^1H 7.54 (dd, J_{HP} = 10.5, J_{HH} = 8.6, 3*o*-C$_6$H$_4$), 7.41 (dd, J_{HP} = 2.0, J_{HH} = 8.6, 3*m*-C$_6$H$_4$), 2.94 (d, J_{HP} = 2.4, ≡CH), 1.71 (s, C$_5$(CH$_3$)$_5$), 1.32 (s, 3ArC(CH$_3$)$_3$); $^{13}C\{^1H\}$ 153.7 (d, J_{CP} = 2.3, *p*-C$_6$H$_4$), 134.4 (d, J_{CP} = 10.9, *o*-C$_6$H$_4$), 132.9 (d, J_{CP} = 52.0, *i*-C$_6$H$_4$), 125.5 (d, J_{CP} = 10.4, *m*-C$_6$H$_4$), 111.7 (s, ≡CH), 100.5 (d, J_{CP} = 1.9, *C*$_5$(CH$_3$)$_5$), 99.6 (d, J_{CP} = 15.3, ReC≡), 35.2 (s, Ar*C*(CH$_3$)$_3$), 31.5 (s, ArC(*C*H$_3$)$_3$), 10.3 (s, *C*$_5$(CH$_3$)$_5$); $^{31}P\{^1H\}$ 16.2 (s).

[(η^5-C$_5$Me$_5$)Re(NO)(P(4-C$_6$H$_4$-*t*-C$_4$H$_9$)$_3$)(HC≡CC≡CSiMe$_3$)]$^+$BF$_4^-$ (6c$^+$BF$_4^-$). The complex **1c** (0.204 g, 0.256 mmol), chlorobenzene (ca. 10 mL), HBF$_4$·OEt$_2$ (0.047 mL, 0.28 mmol), and HC≡CC≡CSiMe$_3$ (0.11 g, 0.28 mmol) were combined in a procedure analogous to that for **6b**$^+$BF$_4^-$. An identical workup gave **6c**$^+$BF$_4^-$ as a light tan powder (0.224 g, 0.226 mmol, 88%), mp 141−150 °C dec. Anal. Calcd for $C_{47}H_{64}BF_4NOPReSi$: C, 56.96; H, 6.51. Found: C, 55.88; H, 6.39.[36] IR:[28] $\nu_{C\equiv C}$ 2139 w, ν_{NO} 1704 vs. MS:[29] 904 (**6c**$^+$, 100%).

NMR (CD$_2$Cl$_2$):[30] ^1H (major/minor rotamer) 7.71−7.01 (m, 3C$_6$H$_4$), 7.19/8.29 (2 d, J_{HP} = 19.5/4.5, ≡CH syn/anti to PR$_3$),[34] 1.81/1.75 (2 s, C$_5$(CH$_3$)$_5$), 1.38/1.30 (2 s, 3ArC(CH$_3$)$_3$), 0.36/−0.43 (2 s, Si(CH$_3$)$_3$); $^{13}C\{^1H\}$ (major rotamer) 157.4−155.7 (m, *p*-C$_6$H$_4$), 134.0 (br s, *o*-C$_6$H$_4$), 133.2 (br s, *i*-C$_6$H$_4$), 127.0 (br s, *m*-C$_6$H$_4$), 114.8 (s, *C*≡CSi), 110.5 (s, *C*$_5$(CH$_3$)$_5$), 98.1 (d, J_{CP} = 18, H*C*≡C syn to PR$_3$),[34] 95.2 (s, C≡*C*Si), 92.5 (d, J_{CP} = 3.5, HC≡*C* anti to PR$_3$),[34] 35.6 (s, Ar*C*(CH$_3$)$_3$), 31.3 (s, ArC(*C*H$_3$)$_3$), 9.7 (s, C$_5$(*C*H$_3$)$_5$), −0.26 (s, Si(CH$_3$)$_3$); $^{31}P\{^1H\}$ 19.0/14.2 (2 s, 5:95).

(η^5-C$_5$Me$_5$)Re(NO)(P(4-C$_6$H$_4$-*t*-C$_4$H$_9$)$_3$)(C≡CC≡CSiMe$_3$) (7c). The complex **6c**$^+$BF$_4^-$ (0.116 g, 0.117 mmol), THF (ca. 9 mL), and *t*-BuOK (1 M in THF; 0.140 mL, 0.140 mmol) were combined in a procedure analogous to that for **7b**. An identical workup (extraction with 3 mL of benzene) gave **7c** as an orange powder (0.088 g, 0.097 mmol, 83%), mp 197−220 °C dec (no melting; orange/ brown/black color transition). IR:[28] $\nu_{C\equiv C}$ 2113 m, 2093 s, ν_{NO} 1646 vs. MS:[29] 903 (**7c**$^+$, 100%).

NMR (CD$_2$Cl$_2$):[30] ^1H 7.58−7.36 (m, 3C$_6$H$_4$), 1.71 (s, C$_5$(CH$_3$)$_5$), 1.32 (s, 3ArC(CH$_3$)$_3$), 0.13 (s, Si(CH$_3$)$_3$); $^{13}C\{^1H\}$ 154.0 (d, J_{CP} = 2.1, *p*-C$_6$H$_4$), 134.2 (d, J_{CP} = 11.1, *o*-C$_6$H$_4$), 132.2 (d, J_{CP} = 55.0, *i*-C$_6$H$_4$), 125.7 (d, J_{CP} = 10.5, *m*-C$_6$H$_4$), 111.4 (s, ReC≡*C*),[34] 108.0 (d, J_{CP} = 15.4, Re*C*≡C),[34] 101.3 (d, J_{CP} = 1.5, *C*$_5$(CH$_3$)$_5$), 92.4 (d, J_{CP} = 2.1, *C*≡CSi),[34] 80.7 (d, J_{CP} = 1.3, C≡*C*Si),[34] 35.2 (s, Ar*C*(CH$_3$)$_3$), 31.5 (s, ArC(*C*H$_3$)$_3$), 10.2 (s, C$_5$(*C*H$_3$)$_5$), 0.89 (s, Si(CH$_3$)$_3$); $^{31}P\{^1H\}$ 16.3 (s).

(η^5-C$_5$Me$_5$)Re(NO)(P(4-C$_6$H$_4$-*t*-C$_4$H$_9$)$_3$)(C≡CC≡CH) (8c). A Schlenk flask was charged with **7c** (0.051 g, 0.055 mmol), THF (7 mL), and *n*-Bu$_4$N$^+$F$^-$ (1.0 M in THF/5 wt % H$_2$O; 0.011 mL, 0.011 mmol). The mixture was stirred for 1 h. The solvent was removed by rotary evaporation and oil pump vacuum, and THF (5 mL) was added. The solution was filtered through silica (2 cm). The solvent was removed from the filtrate by rotary evaporation. Hexane (4 mL) was added to the oil, and the solvent was removed by rotary evaporation and oil pump vacuum to give **8c** as an orange powder (0.040 g, 0.048 mmol, 88%), mp 185−209 °C dec (no melting; orange/black color transition).[19] Anal. Calcd for $C_{44}H_{55}NOPRe$: C, 63.59; H, 6.67. Found: C, 63.87; H, 7.04. IR:[28] $\nu_{C\equiv C}$ 2113 s, 1974 vw, ν_{NO} 1643 vs. MS:[29] 831 (**8c**$^+$, 100%).

NMR (C$_6$D$_6$):[30] ^1H 7.84 (dd, J_{HP} = 10.8, J_{HH} = 8.6, 3*o*-C$_6$H$_4$), 7.20 (dd, J_{HP} = 2.0, J_{HH} = 8.6, 3*m*-C$_6$H$_4$), 1.99 (d, J_{HP} = 0.7, ≡CH), 1.64 (s, C$_5$(CH$_3$)$_5$), 1.12 (s, 3ArC(CH$_3$)$_3$); $^{13}C\{^1H\}$ 153.6 (d, J_{CP} = 2.3, *p*-C$_6$H$_4$), 134.8 (d, J_{CP} = 10.9, *o*-C$_6$H$_4$), 133.1 (d, J_{CP} = 53.4, *i*-C$_6$H$_4$), 125.8 (d, J_{CP} = 10.5, *m*-C$_6$H$_4$), 111.3 (s, ReC≡*C*),[34] 103.0 (d, J_{CP} = 15.9, Re*C*≡C),[34] 100.8 (d, J_{CP} = 1.7, *C*$_5$(CH$_3$)$_5$), 73.0 (d, J_{CP} = 2.8, *C*≡CH),[34] 65.4 (s, C≡*C*H),[34] 35.0 (s, Ar*C*(CH$_3$)$_3$) 31.5 (s, ArC(*C*H$_3$)$_3$), 10.3 (s, C$_5$(*C*H$_3$)$_5$); $^{31}P\{^1H\}$ 17.2 (s).

(η^5-C$_5$Me$_5$)Re(NO)(P(4-C$_6$H$_4$-*t*-C$_4$H$_9$)$_3$)(C≡C)$_4$((4-*t*-C$_4$H$_9$-C$_6$H$_4$)$_3$P)(ON)Re(η^5-C$_5$Me$_5$) (9c). A Schlenk flask was charged with **8c** (0.350 g, 0.422 mmol), Cu(OAc)$_2$ (0.091 g, 0.51 mmol), and pyridine (ca. 8 mL). The mixture was stirred for 0.5 h at 55 °C. The solvent was removed by oil pump vacuum, and benzene (5 mL) was added. The mixture was filtered through Celite (2 cm). The solvent was removed by rotary evaporation. The sample was passed through base-washed Florisil (6 cm, THF/hexane, 1:1). The solvent was removed by rotary evaporation. The oil was dissolved in CH$_2$Cl$_2$ (2 mL), and hexane (10 mL) was added. The solvent was removed by rotary evaporation and oil pump vacuum to give **9c** as a dark red powder (0.190 g, 0.114 mmol, 54%; 75:25 diastereomer mixture), mp 245−260 °C dec (no melting; orange/brown/black color transition). A second CH$_2$Cl$_2$/hexanes precipitation gave a 95:5 diastereomer mixture. Anal. Calcd for $C_{88}H_{108}N_2O_2P_2Re_2$: C, 63.67; H, 6.56. Found: C, 63.76; H, 6.60. IR:[28] $\nu_{C\equiv C}$ 2108 s, 1954 m, ν_{NO} 1642 vs. UV−vis[33] (6.56 × 10^{-6} M): 232 (90 200), 362 (65 600), 394 (61 000). MS:[29] 1661 (**9c**$^+$, 100%).

NMR (C$_6$D$_6$):[30] ^1H 7.83 (dd, J_{HP} = 10.8, J_{HH} = 8.1, 3*o*-C$_6$H$_4$), 7.25 (dd, J_{HP} = 1.7, J_{HH} = 8.1, 3*m*-C$_6$H$_4$), 1.64, 1.62 (2 s, 5:95, C$_5$(CH$_3$)$_5$), 1.14, 1.12 (2 s, 97:3, 3ArC(CH$_3$)$_3$); $^{13}C\{^1H\}$ 153.6 (d, J_{CP} = 2.1, *p*-C$_6$H$_4$), 134.8 (d, J_{CP} = 10.9, *o*-C$_6$H$_4$), 132.9 (d, J_{CP} = 53.8, *i*-C$_6$H$_4$), 125.8 (d, J_{CP} = 10.5, *m*-C$_6$H$_4$), 114.5 (s, ReC≡*C*), 110.3 (d, J_{CP} = 15, Re*C*≡C), 101.0 (s, *C*$_5$(CH$_3$)$_5$), 67.7 (d, J_{CP} = 3.0, ReC≡C*C*), 66.0 (s, ReC≡CC≡*C*), 35.0 (s, Ar*C*(CH$_3$)$_3$), 31.6 (s, ArC(*C*H$_3$)$_3$), 10.3 (s, C$_5$(*C*H$_3$)$_5$); $^{31}P\{^1H\}$ 17.2, 17.0 (2 s, 5:95).

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[35] Similar conditions were used to prepare [(η^5-C$_5$Me$_5$)Re(NO)(P(c-C$_6$H$_{11}$)$_3$)(HC≡CH)]$^+$BF$_4^-$ (**2e**$^+$BF$_4^-$) and (η^5-C$_5$Me$_5$)Re(NO)(P(c-C$_6$H$_{11}$)$_3$)-(C≡CH) (**3e**). These compounds were obtained in spectroscopically pure form but only partially characterized due to the lack of successful coupling chemistry. Key data follow. **2e**$^+$BF$_4^-$: IR[28] ν_{NO} 1699 vs; MS[29] 658 (**2e**$^+$, 100%); NMR (CDCl$_3$)[30] ^1H 7.48 (d, J_{HP} = 4.8, HC≡ anti to PR$_3$),[31] 7.17 (d, J_{HP} = 14.4, HC≡ syn to PR$_3$),[31] 2.04 (s, C$_5$(CH$_3$)$_5$), $^{31}P\{^1H\}$ 20.7 (s). **3d**: IR[28] $\nu_{C\equiv C}$ 1933 m, ν_{NO} 1627 vs; NMR (CDCl$_3$) ^1H 2.98 (d, J_{HP} = 2.4, ≡CH), 1.88 (s, C$_5$(CH$_3$)$_5$), $^{31}P\{^1H\}$ 18.6 (s).

[36] Precipitation from CH$_2$Cl$_2$/hexane gave a CH$_2$Cl$_2$ solvate that gave somewhat better analyses. Anal. Calcd for $C_{47}H_{64}BF_4NOPReS\cdot 0.5CH_2Cl_2$: C, 55.20; H, 6.34. Cl, 3.43. Found: C, 55.25; H, 6.40. Cl, 2.19.

$[(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(P(4-C}_6\text{H}_4\text{C}_6\text{H}_5)_3)(\text{HC}{\equiv}\text{CC}{\equiv}\text{CSiMe}_3)]^+\text{BF}_4^-$ (6d$^+$BF$_4^-$). The complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)}(\text{P(4-C}_6\text{H}_4\text{C}_6\text{H}_5)_3)(\text{CH}_3)$ (**1d**;[12] 0.154 g, 0.179 mmol), chlorobenzene (ca. 5 mL), $\text{HBF}_4\cdot\text{OEt}_2$ (0.025 mL, 0.18 mmol), and $\text{HC}{\equiv}\text{CC}{\equiv}\text{CSiMe}_3$ (0.060 g, 0.530 mmol) were combined in a procedure analogous to that for **6b**$^+\text{BF}_4^-$. An identical workup gave **6d**$^+\text{BF}_4^-$ as a light tan powder (0.135 g, 0.128 mmol, 71%), mp 159−161 °C dec. Anal. Calcd for $\text{C}_{53}\text{H}_{52}\text{BF}_4\text{NOPReSi}$: C, 60.57; H, 4.99; N, 1.33. Found: C, 59.82; H, 5.02; N, 1.28.[37] IR:[28] $\nu_{\text{C}\equiv\text{C}}$ 2141 w, ν_{NO} 1703 vs. MS:[29] 964 (**6d**$^+$, 100%), 842 ($((\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)}(\text{P(C}_6\text{H}_4\text{C}_6\text{H}_5)_3))^+$, 24%); no other peaks above 400 of >4%.

NMR (CD_2Cl_2):[30] ^{1}H (major/minor rotamer) 8.0−7.3 (m, $3\text{C}_6\text{H}_4\text{C}_6\text{H}_5$), 7.26/8.36 (2 d, J_{HP} = 19.5/4.5, $\equiv$CH syn/anti to PR_3),[34] 1.94/1.86 (2 s, $\text{C}_5(\text{CH}_3)_5$), 0.37/-0.39 (2 s, $\text{Si(CH}_3)_3$); $^{13}\text{C}\{^1\text{H}\}$ (major rotamer) 146.5 (d, J_{CP} = 2.7, *p*-C_6H_4), 139.6 (s, *i*-C_6H_5), 134.9 (d, J_{CP} = 10.6, *o*-C_6H_4), 129.9−127.5 (m, *i,p*-C_6H_4, *o,m,p*-C_6H_5), 115.4 (s, $\mathit{C}{\equiv}\text{CSi}$), 110.7 (s, $\mathit{C}_5(\text{CH}_3)_5$), 97.1 (d, J_{CP} = 18.1, $\text{H}\mathit{C}{\equiv}\text{C}$ syn to PR_3),[34] 95.5 (s, $\text{C}{\equiv}\mathit{C}\text{Si}$), 92.4 (d, J_{CP} = 3.7, $\text{HC}{\equiv}\mathit{C}$ anti to PR_3),[34] 9.9 (s, $\text{C}_5(\mathit{C}\text{H}_3)_5$), −0.3 (s, $\text{Si(CH}_3)_3$); $^{31}\text{P}\{^1\text{H}\}$ 20.2/15.3 (2 s, 14:86).

$(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(P(4-C}_6\text{H}_4\text{C}_6\text{H}_5)_3)(\text{C}{\equiv}\text{CC}{\equiv}\text{CSiMe}_3)$ (7d). The complex **6d**$^+\text{BF}_4^-$ (0.113 g, 0.107 mmol), THF (ca. 5 mL), and *t*-BuOK (1.0 M in THF; 0.13 mL, 0.13 mmol) were combined in a procedure analogous to that for **7b**. An identical workup gave **7d** as an orange powder (0.085 g, 0.088 mmol, 82%), mp 165−167 °C dec. Anal. Calcd for $\text{C}_{53}\text{H}_{51}\text{NOPReSi}$: C, 66.09; H, 5.34; N, 1.45. Found: C, 65.97; H, 5.23; N, 1.45.[38] IR:[28] $\nu_{\text{C}\equiv\text{C}}$ 2114 s, 2097 s, ν_{NO} 1649 vs. MS:[29] 963 (**7d**$^+$, 100%).

NMR (C_6D_6):[30] ^{1}H 7.92 (dd, J_{HP} = 11.0, J_{HH} = 8.7, 3*o*-C_6H_4), 7.48−7.36, 7.23−7.07 (2 m, $3\text{C}_6\text{H}_4\text{C}_6\text{H}_5$), 1.66 (s, $\text{C}_5(\text{CH}_3)_5$), 0.15 (s, $\text{Si(CH}_3)_3$); $^{13}\text{C}\{^1\text{H}\}$ 143.1 (d, J_{CP} = 2.3, *p*-C_6H_4), 140.3 (s, *i*-C_6H_5), 134.9 (d, J_{CP} = 11.0, *o*-C_6H_4), 129.0 (s, *o*-C_6H_5), 127.5 (s, *m*-C_6H_5), 127.2 (d, J_{CP} = 10.6, *m*-C_6H_4), 112.7 (s, $\text{ReC}{\equiv}\mathit{C}$),[34] 105.6 (d, J_{CP} = 15.9, $\text{Re}\mathit{C}{\equiv}\text{C}$),[34] 100.7 (d, J_{CP} = 1.7, $\mathit{C}_5(\text{CH}_3)_5$), 93.4 (d, J_{CP} = 2.6, $\mathit{C}{\equiv}\text{CSi}$),[34] 80.9 (s, $\text{C}{\equiv}\mathit{C}\text{Si}$),[34] 10.0 (s, $\text{C}_5(\mathit{C}\text{H}_3)_5$), 0.8 (s, $\text{Si(CH}_3)_3$); $^{31}\text{P}\{^1\text{H}\}$ 19.6 (s).

$(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(P(4-C}_6\text{H}_4\text{C}_6\text{H}_5)_3)(\text{C}{\equiv}\text{CC}{\equiv}\text{CH})$ (8d). The complex **7d** (0.085 g, 0.088 mmol), THF (3 mL), and *n*-$\text{Bu}_4\text{N}^+\text{F}^-$ (1.0 M in THF/5 wt % H_2O; 0.017 mL, 0.017 mmol) were combined in a procedure analogous to that for **8c**. A nearly identical workup (extraction with 3 mL of THF; final precipitation/evaporation from 4 mL of hexane and 1 mL of CH_2Cl_2) gave **8d** as an orange powder (0.048 g, 0.054 mmol, 61%), mp 245−247 °C dec.[19] Anal. Calcd for $\text{C}_{50}\text{H}_{43}\text{NOPRe}$: C, 67.40; H, 4.86. Found: C, 67.49; H, 4.88. IR:[28] $\nu_{\text{C}\equiv\text{C}}$ 2114 s, 1975 vw, ν_{NO} 1649 vs. MS:[29] 892 (**8d**$^+$, 95%), 842 ($((\text{C}_5\text{Me}_5)\text{Re(NO)}(\text{P(C}_6\text{H}_4\text{C}_6\text{H}_5)_3))^+$, 100%).

NMR (CD_2Cl_2):[30] ^{1}H 7.82−7.30 (m, $3\text{C}_6\text{H}_4\text{C}_6\text{H}_5$), 2.06 (s, $\equiv$CH), 1.80 (s, $\text{C}_5(\text{CH}_3)_5$); $^{13}\text{C}\{^1\text{H}\}$ 143.1 (d, J_{CP} = 2.3, *i*-C_6H_5), 140.3 (s, *p*-C_6H_5), 134.9 (d, J_{CP} = 11.2, *o*-C_6H_4), 134.3 (d, J_{CP} = 52.9, *i*-C_6H_4), 133.1 (d, J_{CP} = 10.1, *p*-C_6H_4), 129.0 (s, *m*-C_6H_5), 127.4 (s, *o*-C_6H_5), 127.1 (d, J_{CP} = 10.6, *m*-C_6H_4), 111.3 (s, $\text{ReC}{\equiv}\mathit{C}$),[34] 102.0 (d, J_{CP} = 16.3, $\text{Re}\mathit{C}{\equiv}\text{C}$),[34] 100.6 (s, $\text{C}_5(\text{CH}_3)_5$), 72.4 (d, J_{CP} = 2.8, $\mathit{C}{\equiv}\text{CH}$),[34] 65.4 (s, $\text{C}{\equiv}\mathit{C}\text{H}$),[34] 10.0 (s, $\text{C}_5(\mathit{C}\text{H}_3)_5$); $^{31}\text{P}\{^1\text{H}\}$ 18.4 (s).

$(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(P(4-C}_6\text{H}_4\text{C}_6\text{H}_5)_3)(\text{C}{\equiv}\text{C})_4((\text{4-C}_6\text{H}_5\text{C}_6\text{H}_4)_3\text{P)(ON)Re}(\eta^5\text{-C}_5\text{Me}_5)$ (9d). The complex **8d** (0.361 g, 0.405 mmol), Cu(OAc)_2 (0.085 g, 0.47 mmol), and pyridine (ca. 8 mL) were combined in a procedure analogous to that given for **9c**. A similar workup (Florisil replaced by silica, 2−3 cm, THF/hexane, 1:1) gave **9d** as a dark red powder (0.147 g, 0.0825 mmol, 40%; 71:29 diastereomer mixture), mp 240−243 °C dec. A second CH_2Cl_2/hexanes precipitation gave a 96:4 diastereomer mixture. Anal. Calcd for $\text{C}_{100}\text{H}_{84}\text{N}_2\text{O}_2\text{P}_2\text{Re}_2$: C, 67.47; H, 4.76. Found: C, 67.40; H 4.83. IR:[28] $\nu_{\text{C}\equiv\text{C}}$ 2108 s, 1954 m, ν_{NO} 1642 vs. UV−vis[33] (7.25×10^{-6} M) 228 (74 500), 270 (164 000), 362 (74 200), 392 (61 000). MS:[29] 1780 (**9d**$^+$, 100%), 842 ($((\text{C}_5\text{Me}_5)\text{Re(NO)}(\text{P(C}_6\text{H}_4\text{C}_6\text{H}_5)_3))^+$, 35%); no other peaks above 400 of >13%.

NMR (C_6D_6):[30] ^{1}H 7.92 (dd, J_{HP} = 10.5, J_{HH} = 8.1, 3*o*-C_6H_4), 7.45−7.36, 7.22−7.07 (2 m, remaining $3\text{C}_6\text{H}_4\text{C}_6\text{H}_5$), 1.68, 1.63 (2 s, 4:96, $\text{C}_5(\text{CH}_3)_5$); $^{13}\text{C}\{^1\text{H}\}$ 143.2 (d, J_{CP} = 2.3, *i*-C_6H_5), 140.4 (s, *p*-C_6H_5), 134.9 (d, J_{CP} = 11.2, *o*-C_6H_4), 134.9 (d, J_{CP} = 50.1, *i*-C_6H_4), 133.1 (d, J_{CP} = 10.1, *p*-C_6H_4), 129.0 (s, *o*-C_6H_5), 127.6 (s, *m*-C_6H_5), 127.2 (d, J_{CP} = 10.6, *m*-C_6H_4), 114.4 (s, $\text{ReC}{\equiv}\mathit{C}$), 109.8 (d, J_{CP} = 16.9, $\text{Re}\mathit{C}{\equiv}\text{C}$), 100.9 (s, $\mathit{C}_5(\text{CH}_3)_5$), 67.5 (s, $\text{ReC}{\equiv}\text{C}\mathit{C}$), 65.8 (s, $\text{ReC}{\equiv}\text{CC}{\equiv}\mathit{C}$), 10.0 (s, $\text{C}_5(\mathit{C}\text{H}_3)_5$); $^{31}\text{P}\{^1\text{H}\}$ 19.2, 18.8 (2 s, 6:94).

$[(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(P(}\mathit{c}\text{-C}_6\text{H}_{11})_3)(\text{HC}{\equiv}\text{CC}{\equiv}\text{CSiMe}_3)]^+\text{BF}_4^-$ (6e$^+$BF$_4^-$). The complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(P(c-C}_6\text{H}_{11})_3)(\text{CH}_3)$ (**1e**;[12] 0.646 g, 1.000 mmol), chlorobenzene (10 mL), $\text{HBF}_4\cdot\text{OEt}_2$ (0.16 mL, 1.0 mmol), and $\text{HC}{\equiv}\text{CC}{\equiv}\text{CSiMe}_3$ (0.122 g, 1.00 mmol) were combined in a procedure analogous to that for **6b**$^+\text{BF}_4^-$. The solvent was removed by oil pump vacuum, and CH_2Cl_2 (5 mL) was added. The solution was filtered through a Celite pad and slowly added to rapidly stirred ether/hexane (150 mL, 1:1 v/v). A light tan powder was collected by filtration, washed with pentane (2 × 30 mL), and air-dried to give **6e**$^+\text{BF}_4^-$ (0.400 g, 0.476 mmol, 48%), mp 80−82 °C dec. IR:[28] $\nu_{\text{C}\equiv\text{C}}$ 2138 w, ν_{NO} 1702 vs. MS:[29] 754 (**6e**$^+$, 100%).

NMR (CDCl_3):[30] ^{1}H (major/minor rotamer) 7.46/8.12 (2 d, J_{HP} = 14.4/4.5, $\equiv$CH anti/syn to PR_3),[34] 2.09/2.04 (2 s, $\text{C}_5(\text{CH}_3)_5$), 2.30−1.20 (br m, 3c-$\text{C}_6\text{H}_{11}$), 0.30/0.26 (2 s, $\text{Si(CH}_3)_3$); $^{13}\text{C}\{^1\text{H}\}$ (major or major/minor rotamer) 113.6 (s, $\mathit{C}{\equiv}\text{CSi}$), 110.3/110.2 (2 s, $\mathit{C}_5(\text{CH}_3)_5$), 96.6 (s, $\text{C}{\equiv}\mathit{C}\text{Si}$), 93.7/92.9 (2d, J_{CP} = 18/3.5, $\text{H}\mathit{C}{\equiv}\text{C}$ syn/anti to PR_3),[34] 38.1 (d, J_{CP} = 24.3 Hz, $\text{P}\mathit{C}\text{H}$), 30.7 (br s, CH_2), 30.4 (br s, CH_2), 27.7 (br s, CH_2), 27.6 (br s, CH_2), 26.0 (s, CH_2), 10.42/10.46 (2 s, $\text{C}_5(\mathit{C}\text{H}_3)_5$), −0.22/-0.26 (2 s, $\text{Si(CH}_3)_3$); $^{31}\text{P}\{^1\text{H}\}$ 21.0/16.5 (2 s, 14:86).

$(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(P(}\mathit{c}\text{-C}_6\text{H}_{11})_3)(\text{C}{\equiv}\text{CC}{\equiv}\text{CSiMe}_3)$ (7e). The complex **6e**$^+\text{BF}_4^-$ (0.226 g, 0.268 mmol), THF (10 mL), and *t*-BuOK (1 M in THF; 0.045 mL, 0.045 mmol) were combined in a procedure analogous to that for **7b**. An identical workup (extraction with 4 mL of benzene) gave **7e** as a spectroscopically pure red-orange powder (0.180 g, 0.239 mmol, 80%), mp 132 °C slow dec. IR:[28] $\nu_{\text{C}\equiv\text{C}}$ 2115 m, 2097 s, ν_{NO} 1646 vs. MS:[29] 753 (**7e**$^+$, 100%).

NMR (C_6D_6):[30] ^{1}H 2.50−1.20 (br m, 3c-C_6H_{11}), 1.77 (s, $\text{C}_5(\text{CH}_3)_5$), 0.22 (s, $\text{Si(CH}_3)_3$); $^{13}\text{C}\{^1\text{H}\}$ 113.0 (s, $\text{ReC}{\equiv}\mathit{C}$),[34] 107.8 (d, J_{CP} = 16.1, $\text{Re}\mathit{C}{\equiv}\text{C}$),[34] 100.2 (s, $\mathit{C}_5(\text{CH}_3)_5$), 94.0 (d, J_{CP} = 2.3, $\mathit{C}{\equiv}\text{CSi}$),[34] 81.2 (s, $\text{C}{\equiv}\mathit{C}\text{Si}$),[34] 37.6 (d, J_{CP} = 25.1 Hz, $\text{P}\mathit{C}\text{H}$), 30.9 (s, CH_2), 30.2 (s, CH_2), 28.3 (d, J_{CP} = 11.9, CH_2), 28.1 (d, J_{CP} = 9.0, CH_2), 27.2 (s, CH_2), 11.1 (s, $\text{C}_5(\mathit{C}\text{H}_3)_5$), 1.3 (s, $\text{Si(CH}_3)_3$); $^{31}\text{P}\{^1\text{H}\}$ 21.3 (s).

$(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(P(c-C}_6\text{H}_{11})_3)(\text{C}{\equiv}\text{CC}{\equiv}\text{CH})$ (8e). The complex **7e** (0.180 g, 0.239 mmol), K_2CO_3 (0.050 g, 0.36 mmol), and methanol (10 mL) were combined in a procedure analogous to that for **8b**. An identical workup gave **8e** as a spectroscopically pure orange powder (0.150 g, 0.220 mmol, 92%). IR:[28] $\nu_{\text{C}\equiv\text{C}}$ 2110 s, ν_{NO} 1637 vs. MS:[29] 681 (**8e**$^+$, 100%).

NMR (CD_2Cl_2):[30] ^{1}H 2.10−1.10 (br m, 3c-C_6H_{11} and $\equiv$CH), 1.88 (s, $\text{C}_5(\text{CH}_3)_5$); $^{13}\text{C}\{^1\text{H}\}$ 110.5 (s, $\text{ReC}{\equiv}\mathit{C}$),[34] 104.9 (d, J_{CP} = 16.0, $\text{Re}\mathit{C}{\equiv}\text{C}$),[34] 100.1 (s, $\mathit{C}_5(\text{CH}_3)_5$), 72.2 (s, $\mathit{C}{\equiv}\text{CH}$),[34] 64.8 (s, $\text{C}{\equiv}\mathit{C}\text{H}$),[34] 37.1 (d, J_{CP} = 25.1 Hz, $\text{P}\mathit{C}\text{H}$), 30.3 (s, CH_2), 29.7 (s, CH_2), 28.0 (s, CH_2), 27.9 (s, CH_2), 27.7 (s, CH_2), 11.0 (s, $\text{C}_5(\mathit{C}\text{H}_3)_5$); $^{31}\text{P}\{^1\text{H}\}$ 20.0 (s).

$(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(P(}\mathit{c}\text{-C}_6\text{H}_{11})_3)(\text{C}{\equiv}\text{C})_4((\text{c-C}_6\text{H}_{11})_3\text{P)(ON)Re}(\eta^5\text{-C}_5\text{Me}_5)$ (9e). A Schlenk flask was charged with **8e** (0.130 g, 0.191 mmol), Cu(OAc)_2 (0.038 g, 0.21 mmol), and pyridine (10 mL). The mixture was stirred for 1 h at 80 °C. The solvent was removed by oil pump vacuum, and benzene (6 mL) was added. The solution was chromatographed on silica

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(37) The sample for microanalysis was additionally precipitated from acetone/hexane and dried under oil pump vacuum. Precipitation from CH_2Cl_2/hexane gave a sample that was believed from NMR to be a hemisolvate but analyzed better for but the microanalysis was in better agreement with $\text{C}_{53}\text{H}_{52}\text{BF}_4\text{NOPSiRe}\cdot0.3\text{CH}_2\text{Cl}_2$. Anal. Calcd: C, 59.46; H, 4.92. Cl, 1.97. Found: C, 59.03; H, 4.89. Cl, 1.92.

(38) The sample for microanalysis was filtered through Alox (neutral; Fluka) in place of Celite.

(benzene). The orange band was collected, and solvent was removed by oil pump vacuum to give **9e** as an orange powder (0.055 g, 0.040 mmol, 38%), mp 176 °C slow dec. Anal. Calcd for $C_{64}H_{96}N_2O_2P_2Re_2$: C, 56.33; H, 7.12. Found: C, 56.15; H 7.14. IR:[28] $\nu_{C≡C}$ 2110 s, 1953 w, ν_{NO} 1642 vs. UV–vis[33] (1.19×10^{-5} M) 274 (27 300), 340 (39 400), 366 (55 100), 398 (52 800). MS:[29] 1360 (**9e**$^+$, 7%; 100% with respect to peaks above *m*/*e* 500).

NMR (CD_2Cl_2):[30] 2.10–0.70 (br m, 3c-C_6H_{11}), 1.87 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ (C≡C not observed), 100.4 (s, $C_5(CH_3)_5$), 37.1 (d, J_{CP} = 24.5 Hz, PCH), 30.3, 30.2, 29.9, 29.7, 29.6 (overlapping s/d, 3CH_2), 27.8 (br, CH_2), 26.7 (s, CH_2), 10.9 (s, $C_5(CH_3)_5$); $^{31}P\{^1H\}$ 20.4 (s).

Acknowledgment. We thank the U.S. National Science Foundation and the Deutsche Forschungsgemeinschaft (DFG, Grant No. GL 300/1-1) for support.

OM000961M