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Synthesis and properties of chiral rhenium pentatetraenylidene complexes of the formula $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(=C=C=C=C=CAr_2)]^+BF_4^-$ (CAr_2 = 9-fluorenylidene)

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Abstract

The sequential reaction of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CH)$ with *n*-BuLi (one equivalent), 9-fluorenone ($O{=}CAr_2$; 1.5 equivalents), and $Me_3O^+BF_4^-$ (3.0 equivalents) gives thermally labile $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CC(OMe)Ar_2)$ (**2a**) as an orange–red powder in 69% yield. Analogous reactions with 2,7-dichloro- and 2,7-dibromofluorenone give the corresponding complexes **2b**,**c** (68–71%). Treatment of **2a–c** with $BF_3{\cdot}OEt_2$ (one equivalent) gave the title complexes (**3a**–**c**) as labile dark blue powders (79–83%) that exhibited diagnostic cumulenic IR bands ν_{CCC} (1993–1987, 1902–1894 cm^{-1}) and Re=C ^{13}C-NMR signals (256.9 ppm, J_{CP} = 10.8 Hz), and richly featured UV–vis spectra. Attempts to prepare stabile derivatives of **3a**–**c** (additions of phosphines, amines, TCNE; anion metatheses) invariably gave a multitude of products.

Keywords: Rhenium; Cumulenes; 1,3-Dibutadiynyl; Fluorenyl; Pentatetraenylidene

1. Introduction

The interface between organometallic compounds and cumulenes $R_2C{=}(C{=})_xCR_2$ (**I**) poses a variety of fascinating questions and synthetic challenges [1,2]. How are the properties of cumulenes affected when one to four of the terminal substituents (R) are replaced by singly-bonded transition metals (metall**o**cumulenes), as illustrated in **II** (Scheme 1)? How are the properties affected when one or both terminal carbons ($R_2C{=}$) are replaced by doubly bonded transition metals (metall**a**cumulenes), as illustrated in **III**? Monometallic representatives of both groups with two double bonds are well known ($L_nMC(R){=}C{=}CR_2$, $L_nM{=}C{=}CR_2$). However, only a few examples have been reported with five or more double bonds [1–3,3–5]. The metallacumulenes have received somewhat greater attention, probably due to the broad interest in carbene ligands and their intermediacy in important catalytic reactions.

We have isolated and carefully characterized dimetallacumulenes consisting of five double bonds and two chiral rhenium endgroups $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)^+$ (**IV**, Scheme 1) [6,7], and six double bonds and unlike rhenium and manganese endgroups (**V**) [8]. Diiron, diruthenium, and dimanganese analogs of **IV** have been reported by Lapinte et al. [9a], Bruce et al., [9b,c] and Berke et al. [9d]. Very recently, we have isolated dimetallacumulenes with nine double bonds, employing a modified rhenium endgroup [7,10]. In order to rigorously interpret the properties of these compounds, we required monorhenium model complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(=(C=)_xCR_2)]^+X^-$, with *x* as high as possible. Such species had not been previously extended beyond two double bonds ($x = 1$) [11]. Thus, we set out to probe the question of 'how long can the chain go?'

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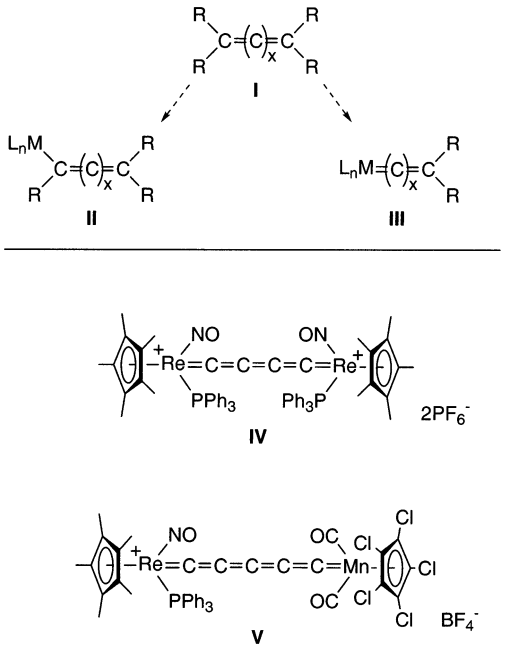
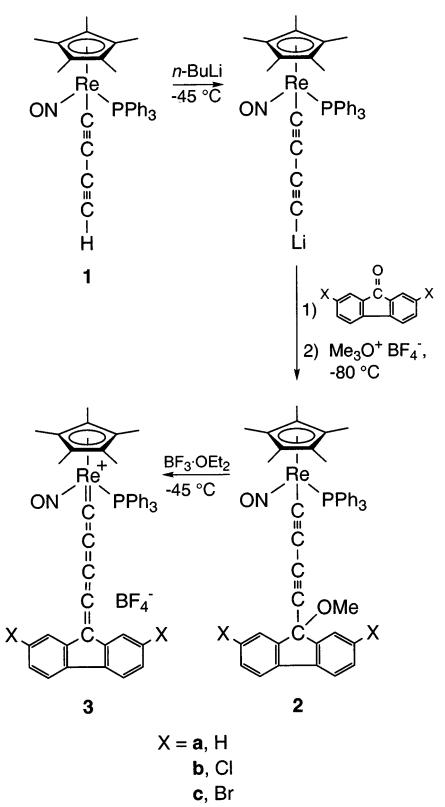
In this endeavor, we followed as unabashed imitators of predecessors who found aryl-substituted carbon termini to be optimal for other metal endgroups [3,5,12]. In this paper, we report the synthesis and isolation of pentatetraenylidene complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(=C=C=C=C=C(aryl)_2)]^+BF_4^-$, where the carbon termini are derived from fluorenone. These are labile at room temperature (r.t.), and can be confidently represented as the longest isolable monometallacumulenes that can be derived from the endgroup $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)^+$.



Scheme 1. Some organometallic cumulene derivatives.



Scheme 2. Syntheses of rhenium pentatetraenylidene complexes.

2. Results

As shown in Scheme 2, the 1,3-butadiynyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CH)$ (**1**) and *n*-BuLi (one equivalent) were combined to give the previously reported lithiated derivative $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CLi)$ [13]. Then fluorenone (1.5 equivalents), henceforth abbreviated as $O{=}CAr_2$, was added. The solution was cooled (-80°C), and $Me_3O^+BF_4^-$ (3.0 equivalents) was added with stirring. Careful workup gave the alkylated butadiynyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CC(OMe)Ar_2)$ (**2a**) as an orange–red powder in 69% yield. Analogous reactions with commercial 2,7-dichlorofluorenone and 2,7-dibromofluorenone ($O{=}C(Ar'X)_2$) gave the corresponding adducts **2b**,**c** (Scheme 2) in 68–71% yields. Reactions with 2,7-dimethylfluorenone, 2,7-dinitrofluorenone, anthrone, dibenzosuberone, benzophenone, and perfluorobenzophenone gave much less stable products.

Compounds **2a**–**c** melted with decomposition slightly above r.t. This visually obvious behavior was further characterized by DSC (Section 4). Mass spectra showed intense parent ions (100–63%), and fragmentation of the methoxy group. After considerable effort, **2b**,**c** were obtained in analytically pure form. Particularly problematic were (1) the separation of excess fluorenone from comparably polar **2a**–**c**, and (2) the tendency of **2a**–**c** to decompose in solution to blue complexes, such as when kept at r.t. in the presence of the excess $Me_3O^+BF_4^-$ (or below r.t. with CH_2Cl_2 cosolvent), or even milder Lewis acids.

The IR spectra of **2a**–**c** (CH_2Cl_2) showed two $\nu_{C\equiv C}$ bands, one medium (2172 cm^{-1}) and the other weak (2018 cm^{-1}), similar to **1** (2115 and 1975 cm^{-1}) and other complexes of the formula $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CR)$ (R = Me, $SiMe_3$; 2193–2118 and 2027–2098 cm^{-1}) [13]. The IR ν_{NO} values of **2a**–**c** (1643–1647 cm^{-1}) and ^{31}P-NMR chemical shifts (19.9–20.3 ppm) were also very close to those of the other 1,3-butadiynyl systems (1644–1653 cm^{-1} and 20.9–21.1 ppm). The ^{13}C-NMR spectra showed $ReC{\equiv}CC{\equiv}C$ signals (δ, THF-d_8) at 107.3–110.4 (d, $J_{CP} = 15.5$–16.1 Hz), 109.8–109.9, 75.5–75.1 (br s or d, $J_{CP} = 3.5$ Hz), and 81.5–81.1, respectively, in accord with previously established chemical shift and coupling constant trends [13,14]. UV–vis spectra were recorded,

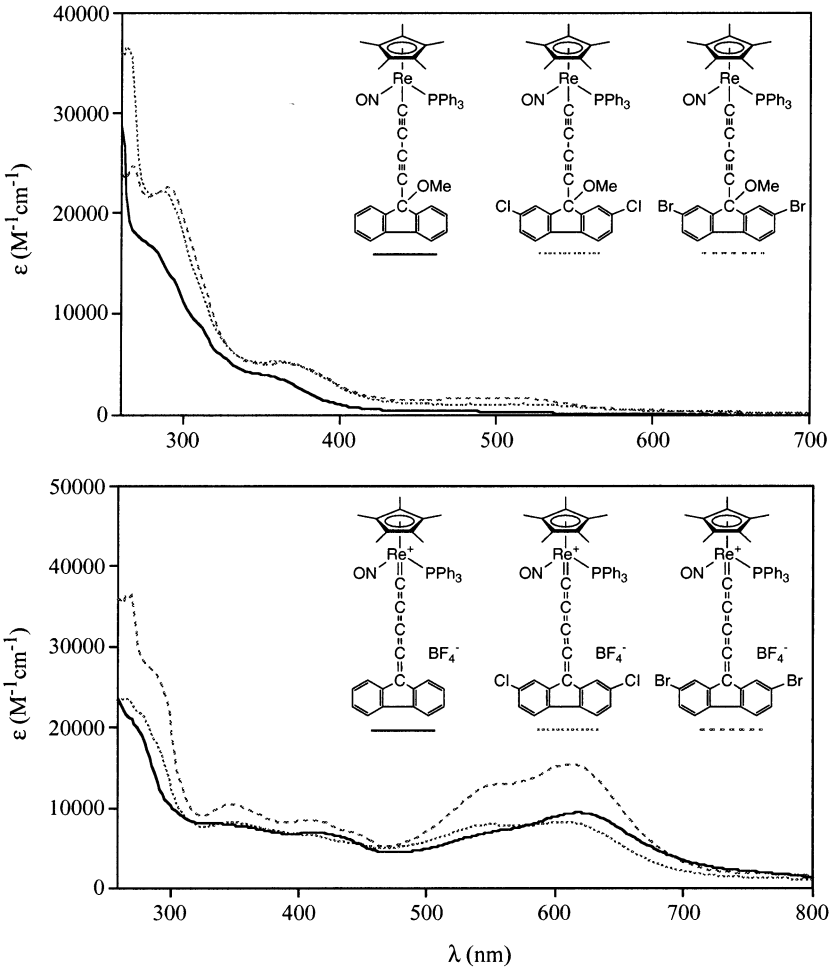


Fig. 1. UV–vis spectra of **2a–c** and **3a–c** (CH_2Cl_2, ambient temperature).

as depicted in Fig. 1. The parent complex **2a** showed a shoulder at 356 nm and a very weak visible absorption at 470 nm. Halide-substituted **2b**,**c** gave more pronounced and red-shifted absorptions (360, 364 nm; 484, 506 nm).

Toluene/hexane solutions of **2a–c** were treated with BF_3OEt_2 (one equivalent) at −45°C. Dark blue solids precipitated immediately. Reprecipitation gave the title compounds $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(=C=C=C=CAr_2)]^+BF_4^-$ (**3a**) and $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(=C=C=C=C=C(Ar'X)_2)]^+BF_4^-$ (**3b**,**c**) in 79–83% yields. Complexes **3a–c** could be stored under nitrogen in a freezer for extended periods, and tolerated brief exposure to air. However, they decomposed without melting slightly above r.t., as characterized by DSC. After considerable effort, **3b** was obtained in analytically pure form. The mass spectrum of **3a** (FAB) gave an intense signal for the parent cation. Befitting their blue color, the UV–vis spectra of **3a–c** showed two quite intense bands at 550–564 and 606–616 nm, and measurable absorption throughout the visible region (Fig. 1). In view of the difficulty in purifying these samples, the extinction coefficients should be regarded as semiquantitative.

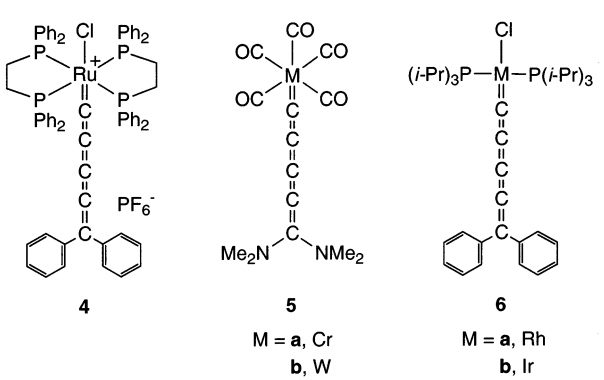
The IR spectra of **3a–c** showed two medium intensity absorptions in a region characteristic of cumulenic ν_{CCC} bands (1993–1987 and 1902–1894 cm^{-1}). Other compounds with M=C=C=C=C=CRR′ linkages exhibit two similar absorptions (2161–1856 cm^{-1}, $\Delta\nu$ 50–100 cm^{-1}) [1,3–5]. The IR ν_{NO} and ^{31}P-NMR values of **3a–c** (1717–1724 cm^{-1} and 21.5–21.6 ppm) were typical of $^+$Re=C systems, including dimetallacumulenes with $^+$Re=C=C=C=M (1701–1717 cm^{-1} and 18.9–20.5 ppm) [8], $^+$Re=C=C=C=C=Re$^+$ (**IV**; 1692–1725 cm^{-1} and 23.6–24.5 ppm) [6], and $^+$Re=C=C=C=C=C=Mn (**V**; 1705–1718 cm^{-1} and 20.5 ppm) [8] linkages. The ^{1}H-NMR spectrum was relatively uninformative. However, the ^{13}C-NMR spectrum of **3a** showed a downfield signal diagnostic of a $^+$Re=C carbon (256.9 ppm), with a $^2J_{CP}$ value close to that of **IV** (10.8 vs. 12.3 Hz). Another downfield signal (176.2 ppm) was assigned to the terminal $=CAr_2$ carbon. Other cumulenic carbon resonances could not be unambiguously located.

With the objective of analytically pure samples or trapping products, other syntheses and reactions were investigated. An excess of BF_3 gas could be employed in place of BF_3OEt_2 in Scheme 2. However, the resulting **3a–c** were of comparable purities. Simple sodium or lithium salts can often abstract leaving groups from atoms bound to electron-rich metal centers under mild conditions [15]. Accordingly, **2b** and excess $Na^+SbF_6^-$ were reacted in CH_2Cl_2 at r.t. After 2 h, the solution turned blue, but the target pentatetrenylidene complex was at best a minor component of the powder isolated. No reaction occurred when **2c** was treated with the 'barf' salt $Na^+B(3,5\text{-}C_6H_3(CF_3)_2)_4^-$ in THF at r.t. Attempts to metathesize **3a–c** to more tractable SbF_6^- or 'barf' salts were also unsuccessful. Reactions of **3a–c** with PMe_3, $PHPh_2$, NEt_3, and TCNE were investigated under a variety of conditions. A multitude of products formed, as assayed by ^{31}P-NMR.

3. Discussion

Complexes **3a–c** join three other classes of pentatetraenylidene complexes that have been previously reported in the literature — the ruthenium, chromium/tungsten, and rhodium/iridium complexes of Touchard and Dixneuf (**4**) [3], Fischer (**5a**,**b**) [4], and Werner (**6a**,**b**) [5] shown in Scheme 3. However, the underlying synthetic strategies differ. As shown in Scheme 2, the cumulenic carbon skeleton of **3a–c** is constructed in the rhenium coordination sphere. In contrast, **4–6** are accessed by coordinating 1,3-butadiyne precursors that contain all needed carbon atoms, such that only a leaving group remains to be abstracted.

When the iridium complex **6b** is not rigorously purified, it decomposes in solution [5a]. Similarly, **4** is stable in THF, but a terminal phenyl ring undergoes electrophilic attack by $^+Ru{=}C{=}C{=}\underline{C}_\gamma$ in $CHCl_3$ [3]. Nonetheless, **4**, **5b**, and **6b** have been crystallographically characterized, and appear to be somewhat more robust than **3a–c**. Complexes **4** and **6a**,**b** lack good ancillary π accepting ligands, so backbonding to the pentatetraenylidene ligand is maximized. Complexes **5a**,**b** provide a similar effect from the opposite direction, with amine donor groups on the carbon terminus and strongly π accepting carbonyl ligands on the metal. However, the pentatetraenylidene ligands in **3a–c** must compete with a strongly π accepting nitrosyl ligand for backbonding, and the halide substituents do not appear sufficient to provide a synergistic electronic effect. Complexes **4–6** also cleanly undergo several types of nucleophile additions, in contrast to our experience with **3a–c**.



4 **5** **6**

M = **a**, Cr
b, W

M = **a**, Rh
b, Ir

Scheme 3. Previously reported pentatetraenylidene complexes.

Complexes **3–6** represent the longest monometallacumulenes reported to date, and **V** (Scheme 1) the longest dimetallacumulene. However, there is good trapping evidence for the C_7 homolog of **5b** [4b]. We studied protonations of the 1,3,5-hexatriynyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CC{\equiv}C\text{-}p\text{-}C_6H_4Me)$ and related compounds in hopes of forming hexapentaenylidene complexes with $^+Re{=}C{=}C{=}C{=}C{=}C{=}CHAr$ linkages [11d]. However, only C_β attack to give vinylidene complexes was observed. A number of cumulenes with two fluorenylidene termini have been reported [16,17]. The longest is the octaheptaene $Ar_2C{=}C{=}C{=}C{=}C{=}C{=}C{=}CAr_2$, solutions of which rapidly decompose below r.t. [17]. Like **3a–c** and **4**, it is blue (λ_{max} (C_6H_6): 540, 597 nm), and the corresponding hexapentaene is also colored (543 nm).

Most of the spectroscopic properties of **2a–c** and **3a–c** follow readily from those of lower homologs. The UV–vis data for **3a–c** in Fig. 1 are the only significant exception. The absorptions in the 500–700 nm region are not an intrinsic property of the fluorene residue, since the are absent in **2a–c**. Hence, they require the metallacumulene. Above 300 nm, the UV–vis spectrum of the parent vinylidene complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(=C{=}CH_2)]^+BF_4^-$ shows only a featureless tail trailing weakly into the visible [11c]. Replacement of one terminal hydrogen by a naphthyl group (C_5H_5 series) gives a moderately intense band at 367 nm (ε 7600), but no additional absorptions [11a]. Thus, the second aryl group and three additional cumulene carbons in **3a–c** cause a marked difference. We suggest that most of the new bands have substantial metal-to-ligand charge transfer character. However, it should be kept in mind (as noted above) that comparable cumulenes with two fluorenylidene endgroups are also colored. Complexes **IV** (392, 574 nm; ε 41 000, 30 000) [6] and **V** (480, 634 nm; ε 60 500, 4800) [8] exhibit more intense visible absorptions than **3a–c**, but not as many features.

In conclusion, we have shown that it is possible to isolate pentatetraenylidene adducts of the chiral rhenium fragment $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)^+$. These are

likely to be the longest monometallacumulenes with this endgroup to show reasonable r.t. stability. However, with bulkier phosphines, significantly longer dirhenacumulenes can be isolated. The properties of pentatetraenylidene complexes **3a**–**c** documented above provide important benchmark data for these upcoming publications [10].

4. Experimental

4.1. General

All reactions and manipulations were conducted under inert atmospheres with standard Schlenk techniques. Instrumentation, solvent purifications, and related data have been described previously [6,8,10]. Reagents were used as received from common commercial sources.

4.2. (η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC≡CC(OMe)Ar_2) (**2a**)

A Schlenk flask was charged with (η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC≡CH) (**1** [10], 0.051 g, 0.077 mmol) and THF (5 ml) and cooled to −45°C (acetonitrile/CO_2). Then *n*-BuLi (0.032 ml, 2.4 M in hexane) was added with stirring. After 1–2 h, fluorenone (O=CAr_2; 0.020 g, 0.12 mmol) was added with stirring. After 0.5 h, the cold bath was removed. After 3 h, the orange solution was cooled to −80°C (acetone/CO_2) and $Me_3O^+BF_4^-$ (0.034 g, 0.230 mmol) was added with stirring. After 0.5 h, the flask was transferred to an ice bath. After 0.25 h, the cold solution was quickly filtered through a frit under N_2 into another Schlenk flask that had been cooled to −80°C. The solvent was removed by oil pump vacuum at low temperature to give orange solid. This was dissolved in a minimum of CH_2Cl_2, and hexane (10 ml) was added. The solvent was removed at 0°C by oil pump vacuum to give an orange–red powder, which was cooled to −80°C. Then CH_2Cl_2 (1 ml) was added. The cold extract was transferred to another cold Schlenk flask removing unreacted 9-fluorenone. Hexane was added (10 ml), and the solvent was removed by oil pump vacuum at 0°C to give **2a** as an orange–red powder (0.046 g, 0.054 mmol, 69%)[1]. DSC (T_i, T_e, T_p)[2] 43/53/84.

IR (cm^{-1}, CH_2Cl_2/C_6H_6/KBr): $\nu_{C\equiv C}$ 2172/2174/2172 m, 2018/2020/2018 w, ν_{NO} 1643/1655/1647 s. NMR (δ): ^1H (CD_2Cl_2/C_6D_6/THF-d_8) 7.70–7.31/7.74–7.36 + 7.12–6.52/7.68–7.22 (m, 23 sp^2-H), 3.15/3.08/3.14 (s, OMe), 1.71/1.61/1.70 (s, C_5Me_5); $^{13}C\{^1H\}$ (THF-d_8, partial) 135.0 (d, J_{CP} = 10.6 Hz, *o*-PPh), 130.8 (s, *p*-PPh), 128.9 (d, J_{CP} = 10.6 Hz, *m*-PPh), 107.3 (d, J_{CP} = 15.5 Hz, Re$\underline{C}$≡), 101.1 (s, $\underline{C}_5(CH_3)_5$), 81.5 (s, ReC≡CC≡$\underline{C}$), 75.5 (s, ReC≡C$\underline{C}$≡C), 52.0 (s, O$\underline{C}H_3$), 10.1 (s, $C_5(\underline{C}H_3)_5$); $^{31}P\{^1H\}$ (CD_2Cl_2/C_6D_6/THF-d_8) 19.9/20.7/20.8 (s). UV–vis (1.1×10^{-4})[3]: 258 (28 800), 280 (16 500), 356 (3800), 470 (400). MS (positive Cs-FAB, 3-NBA/CH_2Cl_2): 858 ($M^+ + 1$, 100%), 826 (M^+–CH_3O, 56%), 663 (M^+ + 1-$C_{14}H_{11}O$, 50%), 614 (M^+–$C_{18}H_{11}O$, 75%); no other peaks above 250 of >30%.

4.3. (η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC≡CC-(OMe)($Ar'Cl)_2$) (**2b**)

Complex **1** (0.062 g, 0.094 mmol), THF (5 ml), *n*-BuLi (0.040 ml, 2.4 M in hexane), 2,7-dichlorofluorenone (O=C($Ar'Cl)_2$; 0.039 g, 0.14 mmol), and $Me_3O^+BF_4^-$ (0.042 g, 0.28 mmol) were combined in a procedure analogous to that for **2a**. A similar workup gave **2b** as an orange–red powder (0.062 g, 0.070 mmol, 71%)[1]. DSC (T_i, T_e, T_p)[2] 56/64/76. Anal. Calc. for $C_{46}H_{39}Cl_2NO_2PRe$: C, 59.67; H, 4.25. Found: C, 59.38; H, 4.33%.

IR (cm^{-1}, CH_2Cl_2/C_6H_6/KBr): $\nu_{C\equiv C}$ 2172/2176/2172 m, 2018/2022/2018 w, ν_{NO} 1647/1655/1649 s. NMR (δ): ^1H (CD_2Cl_2/C_6D_6/THF-d_8) 7.62–7.33/7.80–7.40 + 7.10–6.48/7.88–7.26 (m, 21 sp^2-H), 3.15/3.10/3.19 (s, OMe), 1.72/1.52/1.72 (s, C_5Me_5); $^{13}C\{^1H\}$ (THF-d_8, partial) 134.9 (d, J_{CP} = 11.0 Hz, *o*-PPh), 130.9 (d, J_{CP} = 2.0 Hz, *p*-PPh), 128.9 (d, J_{CP} = 10.1 Hz, *m*-PPh), 110.3 (d, J_{CP} = 16.1 Hz, Re$\underline{C}$≡), 109.8 (s, ReC≡$\underline{C}$), 101.3 (s, $\underline{C}_5(CH_3)_5$), 81.1 (s, ReC≡CC≡$\underline{C}$), 75.1 (s, ReC≡C$\underline{C}$≡C), 52.4 (s, O$\underline{C}H_3$), 10.1 (s, $C_5(\underline{C}H_3)_5$); $^{31}P\{^1H\}$ (CD_2Cl_2/C_6D_6/THF-d_8) 20.1/21.0/20.9 (s). UV–vis (8.6×10^{-5})[3]: 258 (36 000), 264 (36 400), 286 (22 000), 360 (5100), 484 (1000). MS (positive Cs-FAB, 3-NBA/CH_2Cl_2): 926 (M^+, 87%), 663 (M^+–$C_{14}H_9Cl_2O$, 45%), 614 (M^+–$C_{18}H_9Cl_2O$, 100%); no other peaks above 460 of >20%.

4.4. (η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC≡CC-(OMe)($Ar'Br)_2$) (**2c**)

Complex **1** (0.069 g, 0.104 mmol), THF (5 ml), *n*-BuLi (0.044 ml, 2.4 M in hexane), 2,7-dibromofluorenone (O=C($Ar'Br)_2$; 0.054 g, 0.16 mmol), and $Me_3O^+BF_4^-$ (0.046 g, 0.31 mmol) were combined in a procedure analogous to that for **2a**. A similar workup

[1] In some reactions, 1 was observed in the final product. This can be washed out with ether/hexane (1:10 v/v).

[2] T_i, initial peak temperature; T_e, extrapolated peak-onset temperature; T_p, maximum peak temperature, see [18].

[3] All UV–vis spectra were recorded in CH_2Cl_2. Absorbances are in nm (ε, M^{-1} cm^{-1}).

gave **2c** as an orange–red powder (0.072 g, 0.071 mmol, 68%)[1]. DSC (T_i, T_e, T_p)[2] 50/62/72. Anal. Calc. for $C_{46}H_{39}Br_2NO_2PRe$: C, 54.44; H, 3.87. Found: C, 54.22; H, 3.62%.

IR (cm^{-1}, $CH_2Cl_2/C_6H_6/KBr$): $\nu_{C\equiv C}$ 2172/2176/2172 m, 2018/2020/2018 w; ν_{NO} 1647/1655/1647 s. NMR (δ): ^1H (CD_2Cl_2/C_6D_6/THF-d_8): 7.68–7.31/7.78–7.42 + 7.10–6.44/7.84–7.28 (m, 21 sp^2-H), 3.15/3.10/3.18 (s, OMe), 1.71/1.50/1.72 (s, C_5Me_5); $^{13}C\{^1H\}$ (THF-d_8, partial) 134.9 (d, $J_{CP} = 11.0$ Hz, *o*-PPh), 130.9 (s, *p*-PPh), 128.9 (d, $J_{CP} = 10.1$ Hz, *m*-PPh), 110.4 (d, $J_{CP} = 15.5$ Hz, Re$\underline{C}\equiv$), 109.9 (s, ReC$\equiv\underline{C}$), 101.3 (s, $\underline{C}_5(CH_3)_5$), 81.1 (s, ReC$\equiv$CC$\equiv\underline{C}$), 75.2 (d, $J_{CP} = 3.5$ Hz, ReC$\equiv$C$\underline{C}\equiv$C), 52.4 (s, O$\underline{C}H_3$), 10.1 (s, $C_5(\underline{C}H_3)_5$); $^{31}P\{^1H\}$ (CD_2Cl_2/C_6D_6/THF-d_8) 20.3/20.9/20.9 (s). UV–vis (9.5×10^{-5})[3]: 268 (24 500), 290 (22 400), 364 (5000), 506 (1600). MS (positive Cs-FAB, 3-NBA/CH_2Cl_2): 1015 (M^+, 63%), 984 ($M^+ - CH_3O$, 23%), 663 ($M^+ + 1\text{-}C_{14}H_9Br_2O$, 33%), 614 ($M^+ - C_{18}H_9Br_2O$, 100%); no other peaks above 400 of > 30%.

4.5. $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(=C=C=C=C=CAr_2)]^+ BF_4^-$ (3a)

A Schlenk flask was charged with **2a** (0.040 g, 0.047 mmol), toluene (5 ml), and hexane (5 ml) and cooled to −45°C (acetonitrile/CO_2). Then BF_3OEt_2 (0.012 ml, 3.8 M in Et_2O) was added with stirring. A dark blue solid precipitated immediately. The solvent was removed by syringe. The solid was washed with hexane (3×5 ml) and transferred to a Schlenk frit. It was extracted with CH_2Cl_2 (2 ml), leaving an insoluble material. Hexane (10 ml) was added to the extract. The solvent was removed by oil pump vacuum to give **3a** as a fine blue powder (0.034 g, 0.037 mmol, 79%). DSC (T_i, T_e, T_p)[2] 56/66/86.

IR (cm^{-1}, CH_2Cl_2): $\nu_{C\equiv C}$ 1993 m, 1902 m, ν_{NO} 1717 s. NMR (δ, CD_2Cl_2): ^1H 7.80–7.20 (m, 23 sp^2-H), 2.01 (s, C_5Me_5); $^{13}C\{^1H\}$ (partial) 256.9 (d, $J_{CP} = 10.8$, Re=C), 176.2 (s, ReCCCC$\underline{C}$), 133.8 (d, $J_{CP} = 11.1$ Hz, *o*-PPh), 133.0 (s, *p*-PPh), 130.0 (d, $J_{CP} = 11.2$ Hz, *m*-PPh), 111.2 (s, $\underline{C}_5(CH_3)_5$), 10.6 (s, $C_5(\underline{C}H_3)_5$); $^{31}P\{^1H\}$ 21.6 (s). UV–vis (1.1×10^{-4}):[20] 258 (24 700), 270 (21 800), 346 (8200), 412 (7200), 562 (7600), 616 (9800). MS (positive Cs-FAB, 3-NBA/CH_2Cl_2): 826 (M^+, 100%), 614 ($M^+ - C_{18}H_8O$, 93%); no other peaks above 250 of > 25%.

4.6. $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(=C=C=C=C=C\text{-}(Ar'Cl)_2)]^+ BF_4^-$ (3b)

Complex **2b** (0.055 g, 0.059 mmol), toluene (5 ml), hexane (5 ml), and BF_3OEt_2 (0.016 ml, 3.8 M in Et_2O) were combined in a procedure analogous to that for **3a**. A similar workup gave **3b** as a dark blue powder (0.047 g, 0.48 mmol, 81%). DSC (T_i, T_e, T_p)[2] 67/69/79. Anal. Calc. for $C_{45}H_{36}BCl_2F_4NOPRe$: C, 55.06; H, 3.70. Found: C, 54.97; H, 3.51%.

IR (cm^{-1}, CH_2Cl_2): $\nu_{C\equiv C}$ 1987 w, 1894 w, ν_{NO} 1724 s. NMR (δ, CD_2Cl_2): ^1H 7.80–7.20 (m, 21 sp^2-H), 2.03 (s, C_5Me_5); $^{13}C\{^1H\}$ (partial) 133.6 (d, $J_{CP} = 11.6$ Hz, *o*-PPh), 133.1 (s, *p*-PPh), 130.0 (d, $J_{CP} = 11.3$ Hz, *m*-PPh) 111.9 (s, $\underline{C}_5(CH_3)_5$), 10.7 (s, $C_5(\underline{C}H_3)_5$); $^{31}P\{^1H\}$ 21.6 (s). UV–vis (1.1×10^{-4})[3]: 264 (23 700), 280 (21 500), 350 (8200), 408 (6600), 438 (5700), 550 (7900), 606 (8300).

4.7. $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(=C=C=C=C=(Ar'Br)_2)]^+ BF_4^-$ (3c)

Complex **2c** (0.065 g, 0.064 mmol), toluene (5 ml), hexane (5 ml), and BF_3OEt_2 (0.017 ml, 3.8 M in Et_2O) were combined in a procedure analogous to that for **3a**. A similar workup gave **3c** as a dark blue powder (0.057 g, 0.053 mmol, 83%). DSC (T_i, T_e, T_p)[2] 62/65/82. Anal. Calc. for $C_{45}H_{36}BBr_2F_4NOPRe$: C, 50.49; H, 3.39. Found (two samples): C, 49.53/49.46/49.09; H, 4.12/4.18/3.70%.

IR (cm^{-1}, CH_2Cl_2): $\nu_{C\equiv C}$ 1991 m, 1896 m, ν_{NO} 1724 s. NMR (δ, CD_2Cl_2): ^1H 7.90–7.20 (m, 21 sp^2-H), 2.04 (s, C_5Me_5); $^{13}C\{^1H\}$ (partial) 133.6 (d, $J_{CP} = 11.6$ Hz, *o*-PPh), 133.2 (d, $J_{CP} = 2.6$ Hz, *p*-PPh), 130.1 (d, $J_{CP} = 11.3$ Hz, *m*-PPh) 111.9 (s, $\underline{C}_5(CH_3)_5$), 10.7 (s, $C_5(\underline{C}H_3)_5$); $^{31}P\{^1H\}$ 21.5 (s). UV–vis (1.0×10^{-4})[3]: 266 (36 200), 286 (27 300), 350 (10 300), 412 (8400), 442 (6900), 564 (13 000), 612 (15 400).

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References

[1] M.I. Bruce, Chem. Rev. 98 (1998) 2797.
[2] Recent lead references: (a) B. Bildstein, M. Schweiger, H. Kopacka, K.-H. Ongania, K. Wurst, Organometallics 17 (1998) 2414. (b) B. Bildstein, M. Schweiger, H. Angleitner, H. Kopacka, K. Wurst, K.-H. Ongania, M. Fontani, P. Zanello, Organometallics 18 (1999) 4286.
[3] D. Touchard, P. Haquette, A. Daridor, L. Toupet, P.H. Dixneuf, J. Am. Chem. Soc. 116 (1994) 11157.
[4] (a) G. Roth, H. Fischer, Organometallics 15 (1996) 1139. (b) See also G. Roth, H. Fischer, Organometallics 15 (1996) 5766.
[5] (a) R.W. Lass, P. Steinert, J. Wolf, H. Werner, Chem. Eur. J. 2 (1996) 19. (b) I. Kovacik, M. Laubender, H. Werner, Organometallics 16 (1997) 5607.
[6] M. Brady, W. Weng, Y. Zhou, J.W. Seyler, A.J. Amoroso, A.M. Arif, M. Böhme, G. Frenking, J.A. Gladysz, J. Am. Chem. Soc. 119 (1997) 775.

[7] W.E. Meyer, PhD Thesis, University of Utah, 1999.
[8] T. Bartik, W. Weng, J.A. Ramsden, S. Szafert, S.B. Falloon, A.M. Arif, J.A. Gladysz, J. Am. Chem. Soc. 120 (1998) 11071.
[9] (a) N. Le Narvor, L. Toupet, C. Lapinte, J. Am. Chem. Soc. 117 (1995) 7129. (b) M.I. Bruce, L.I. Denisovich, P.J. Low, S.M. Peregudova, N.A. Ustynyuk, Mendeleev Commun. (1996) 200. (c) M.I. Bruce, P.J. Low, K. Coutuas, J.-F. Halet, S.P. Best, G.A. Heath, J. Am. Chem. Soc. 122 (2000) 1949. (d) S. Kheradmandan, K. Heinze, H.W. Schmalle, H. Berke, Angew. Chem. 11 (1999) 2412; Angew. Chem. Int. Ed. Engl. (1999) 2270.
[10] J. Le Bras, W.E. Meyer, J.A. Gladysz, in preparation.
[11] (a) D.R. Senn, A. Wong, A.T. Patton, M. Marsi, C.E. Strouse, J.A. Gladysz, J. Am. Chem. Soc. 110 (1988) 6096. (b) J.A. Ramsden, W. Weng, J.A. Gladysz, Organometallics 11 (1992) 3635. (c) W. Weng, T. Bartik, M.T. Johnson, A.M. Arif, J.A. Gladysz, Organometallics 14 (1995) 889. (d) R. Dembinski, T. Lis, S. Szafert, C.L. Mayne, T. Bartik, J.A. Gladysz, J. Organomet. Chem. 578 (1999) 229.
[12] M. Tamm, T. Jentzsch, W. Werncke, Organometallics 16 (1997) 1418.
[13] W. Weng, T. Bartik, M. Brady, B. Bartik, J.A. Ramsden, A.M. Arif, J.A. Gladysz, J. Am. Chem. Soc. 117 (1995) 11922.
[14] R. Dembinski, T. Bartik, B. Bartik, M. Jaeger, J.A. Gladysz, J. Am. Chem. Soc. 122 (2000) 810.
[15] (a) G.P. Mitchell, T.D. Tilley, J. Am. Chem. Soc. 120 (1998) 7635. (b) S.K. Grumbine, G.P. Mitchell, D.A. Straus, T.D. Tilley, A.L. Rheingold, Organometallics 17 (1998) 5607.
[16] E. Weber, W. Seichter, R.-J. Wang, T.C.W. Mak, Bull. Chem. Soc. Jpn 64 (1991) 659.
[17] R. Kuhn, H. Zahn, Chem. Ber. 84 (1951) 566.
[18] H.K. Cammenga, M. Epple, Angew. Chem. 107 (1995) 1284; Angew. Chem. Int. Ed. Engl. 34 (1995) 1171.