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due to their stability. To utilize the polymer to its full effect (Fig. 1) the precatalyst is first dissolved in methanol, which is subsequently completely removed. This preformation in methanol also has a positive effect on the monomeric SDS due to the better solubility. The polymer effect here, however, does not increase the reactivity as much as in the case of acetal hydrolysis.[6]

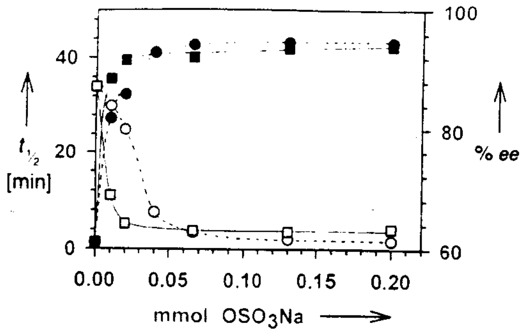

Fig. 1. Hydrogenation of 1 mmol **1f** in 15 mL H_2O in the presence of micelle-forming substances with 0.01 mmol precatalyst **4** (for conditions see Table 1). Open symbols: $t_{1/2}$; filled symbols: % *ee* (*S*); circles: SDS as micelle-forming substance; squares: polymerized micelles with OSO_3Na groups.

The function of the precatalyst **4** is determined by the axial aglycone. As we were recently able to demonstrate, induction of chirality in hydrogenation reactions decreases with an increasing number of axial substituents on the pyranose ring in analagous rhodium(I) chelate complexes of type **3**, which are protected by a benzylidene group in the 4,6-position of the carbohydrate residue.[7] Thus we have now also demonstrated this decrease in optical induction for the first of the conformatively less rigid analogues carrying an axially oriented substituent without the inflexibility imposed by the dioxane ring (Table 2). The enantioselectivity of such conformatively labile seven-membered chelates was shown to be very sensitive to the influences of a modifier.[8, 9] We conjecture that this is a key to direct optical induction over a wide range.

Experimental Procedure

The experimental procedures for the hydrogenation, the synthesis of the precatalyst **2** and the substrates, the derivatization of the hydrogenated products, and the determination of the enantioselectivity are described or referred to in ref. [3], and the synthesis of polymerized micelles in ref. [6]. With polymerized micelles the formation of the catalyst was performed in methanol. For all experiments of Figure 1 and Table 2—but not for those of Table 1—a homogenous solution was made from the precatalyst and the micelle-forming compounds under argon in methanol (5 mL) by stirring for 1 h. The solvent was then removed under vacuum, the dry residue dispersed in water (15 mL) under argon by stirring for 1 h, the substrate added, stirred for 10 min, the argon atmosphere replaced with hydrogen, and the hydrogenation started by stirring. The hydrogenated products were isolated by exhaustive extraction with dichloromethane. For the acid hydrogenation products and the ester from **1f**, the results of the determination of selectivity were additionally checked in double experiments by conversion in methanol to exclude the possibility of enantiomer enrichment during isolation. For this, the hydrogenation suspension was quantitatively evaporated to dryness, and the residue dissolved in methanol. This procedure was also applied to all experiments with the precatalyst **4**. For the enantiomeric excesses determined by gas chromatography, the standard deviation was less than ±1% *ee*; similar results were also obtained for the derivatized hydrogenation products of **1a**, **e**, **h**, and **i**, which were separated by HPLC. To determine the substrate solubility, a small excess of substrate was stirred in water (100 mL) at 25 °C for 1 h, the filtrate evaporated on a watch glass, dried under vacuum, and the residue weighed.

Synthesis of **5**, the glucopyranoside ligand of **3**: A solution of methyl-4,6-*O*-anisylidene-α-D-glucopyranoside (21.78 g, 32 mmol) in pyridine (20 mL) was added to Ph_2PCl (15.53 g, 70.4 mmol) in THF (100 mL) within 5 min with vigorous stirring. Pyridine hydrochloride precipitated out. The next day the solid residue was extracted four times with boiling THF until only the pyridine hydrochloride remained. The pooled solutions were subsequently reduced under vacuum to 50 mL. The target compound crystallized out at 0 °C and was obtained in a very pure form in low yield after recrystallization in anhydrous, oxygen-free toluene/triethylamine (70/30): 10.8 g (33.3%), m.p. 175–178 °C; $[\alpha]_D^{25} = +86.9$ ($c = 2$ in $CHCl_3$); ^{31}P NMR (101.2 MHz, $[D_5]$pyridine, 25 °C): $\delta = 113.6$ (d, $^3J(P,P) = 2.5$ Hz), 116.5 (d, $^3J(P,P) = 2.5$ Hz); ^{13}C NMR (62.8 MHz, $[D_5]$pyridine, 25 °C): $\delta = 54.5$, 54.8 (CH_3, α-CH_3), 62.7 (C6), 68.7 (C2,3,4,5), 99.5 (d, $^3J(C,P) = 6$ Hz; C1), 101.3 (C7) and arene-C signals; correct elemental analysis (C,H,P); MS (70 eV): m/z = 680 ([M^+]).

Synthesis of **4**: [Rh^I(cod)(acac)] (1.55 g, 5 mmol) and **5** (3.4 g, 5 mmol) were dissolved in THF (5 mL) to afford the chelate, and 40% aqueous HBF_4 (10 mmol) added. The yellow solution turned red. After 28 h, of which 10 h were at 65 °C, the solution was filtered to remove impurities. Oxygen-free diethyl ether (40 mL) were stirred into the filtrate, and the complex separated out as an orange syrup. The remaining yellow solution was decanted, and diethyl ether (40 mL) was again added to the oil. The product **4** crystallized out: 4.3 g (89.7%); ^{31}P NMR (101.2 MHz, $CDCl_3$, 25 °C): $\delta = 132.7$ (dd, $^1J(P,Rh) = 178$, $^2J(P,P) = 27$ Hz), 137.3 (dd, $^1J(P,Rh) = 181$, $^2J(P,P) = 27$ Hz); ^{13}C NMR (62.8 MHz, $CDCl_3$, 25 °C): $\delta = 27.9$, 28.9, 30.7, 30.9 (CH_2 of cod), 55.1 (CH_3), 60.9 (C6), 68.7, 70.7, 76.2 ($^3J(C,P) =$ 8 Hz), 80.8 ($^3J(C,P) = 9$ Hz) (C2,3,4,5), 98.3 (d, $^3J(C,P) = 4$ Hz; C1), 101.5, 102.2 (CH of cod), 128.5–134.6 (C-phenyl); LSI-MS (positive, matrix: sulfolane): m/z = 773 [$M^+ - BF_4$], 665 [773 − cod].

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[3] R. Selke, C. Facklam, H. Foken, D. Heller, *Tetrahedron: Asymmetry* **1993**, *4*, 369.

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[5] R. Selke, P. Barthelemy, J. P. Roque, „*Chiral Reactions in Heterogeneous Catalysis*“, ChiCat-Symposium, Brüssel, Oktober 1993.

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[8] D. Seebach et al. have a fascinating example from (taddol)titanium coordination chemistry, in which the induction range extends from 90% *ee* (*R*) to over 90% *ee* (*S*) product: D. Seebach, D. A. Plattner, A. K. Beck, Y. M. Wang, D. Hunzicker, *Helv. Chim. Acta* **1992**, *75*, 2171. Results, deductions, and literature about the dependence of the enantioselectivity on the ligand conformation in analogous catalyst chelate complexes can also be found here.

[9] Investigations have, for example, produced an inversion of the route of induction for a precatalyst analogous to **3** with a 4,6-*O*-benzylidene protective group upon changing to apolar solvents: R. Selke, *J. Prakt. Chem.* **1987**, *329*, 717.

Towards One-Dimensional Carbon Wires Connecting Single Metal Centers: A Cumulenic C_5 Chain that Mediates Charge Transfer between Rhenium and Manganese Termini**

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Compounds in which linear elemental carbon chains span two transition metals, $[L_nMC_xM'L'_n]$, exhibit a variety of unusual physical and chemical properties.[1] However, only complexes with $x = 1-4$ have been isolated to date. We have been particularly interested in charge transfer and electron delocalization across the wire-like C_x moieties[2–4] and have sought to study such phenomena in longer-chain compounds. We reported earlier that C_3 complexes can be prepared by methoxide group ab-

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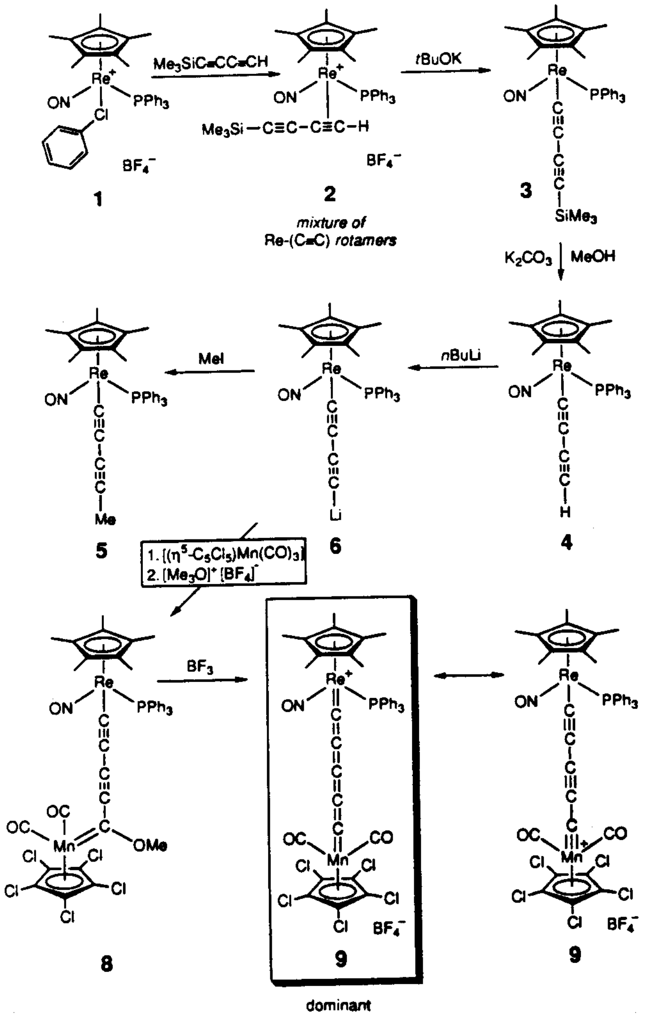
straction from bimetallic Fischer carbene complexes of the formula $[L_nMC{\equiv}CC(OMe){=}M'L'_n]$.[2] These are in turn accessed from $[L_nMC{\equiv}CLi]$ species, metal carbonyl complexes, and $[Me_3O]^+[BF_4]^-$. In this communication, we describe the extension of this methodology to a C_5 complex,[5] which shows several remarkable properties relative to its C_3 counterpart.

The substitution-labile chlorobenzene complex **1**[6] was treated in situ with the 1,3-diyne $HC{\equiv}C{-}C{\equiv}CSiMe_3$. Workup gave the terminal alkyne complex **2** in 95% yield (Scheme 1). Reaction of **2** and *t*BuOK gave the σ complex **3** (96% yield). Protodesilylation (K_2CO_3/CH_3OH) gave the air-stable butadiynyl complex **4** (84% yield), which melted with decomposition at 105–108 °C. Complexes **2**–**4** and other new compounds below were characterized by microanalysis, IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy (Table 1). Most features were similar to those of the monoalkynyl analogues;[7] however, the $\tilde{\nu}$(NO) values in the IR spectrum were 7–20 cm⁻¹ higher, and additional bands assigned to C≡C were observed (2139–1975 cm⁻¹).



Scheme 1. Synthesis of the C_5-bridged bimetallic complex **9**.

Table 1. Selected data for the new compounds:

2: Tan solid, m.p. 118–121 °C (decomp.); ^1H NMR (300 MHz, CD_2Cl_2, 25 °C, CD_2Cl_2 int.): δ = 7.79–7.50 (m, 6H; $3C_6H_5$), 7.48–7.31 (m, 9H; $3C_6H_5$), 7.09/8.24 (major/minor rotamer) (d, *J*(H, P) = 19.7/4.7 Hz, 1H; ≡CH *syn*/*anti* to PPh_3), 1.85/1.77 (s, 15H; $C_5(CH_3)_5$), 0.34/−0.37 (s, 9H; $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 25 °C, CD_2Cl_2 int.): δ = 134.0 (d, *J*(C, P) = 10.7 Hz; *o*-Ph), 133.3 (br s; *p*-Ph), 129.9 (br d, *J*(C, P) = 3.7 Hz; *m*-Ph), 114.9/113.2 (s; *C*≡CSi), 110.3/109.9 (s; $C_5(CH_3)_5$), 92.1/92.9 (d, *J*(C, P) = 3.6/7.0 Hz, HC≡*C*), 96.6/108.0 (d, *J*(C, P) = 18.0/2.4 Hz; H*C*≡C), 95.2/110.4 (s; C≡*C*Si), 9.65 (s; $C_5(CH_3)_5$), −0.51/−0.98 (s; $Si(CH_3)_3$); $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 25 °C, 85% H_3PO_4 ext.): δ = 21.1/17.6 (s, 21:79); IR (CH_2Cl_2/KBr): $\tilde{\nu}$ = 2139/2138(m) (C≡C), 1706/1694(s) cm⁻¹ (NO); MS (positive ions FAB (Cs^+), 3-nitrobenzyl alcohol (3-NBA)/CH_2Cl_2 matrix): *m*/*z* (%) 736 (100) [M^+]. Correct elemental analysis.

3: Orange solid, m.p. 105–108 °C (decomp.); ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = 7.75–7.63 (m, 6H; $3C_6H_5$), 7.04–6.95 (m, 9H; $3C_6H_5$), 1.55 (s, 15H; $C_5(CH_3)_5$), 0.17 (s, 9H; $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C, C_6D_6 int.): δ = 135.3 (d, *J*(C, P) = 51.6 Hz; *i*-Ph), 134.3 (d, *J*(C, P) = 10.7 Hz; *o*-Ph), 130.1 (d, *J*(C, P) = 2.3 Hz; *p*-Ph), 128.4 (d, *J*(C, P) = 10.1 Hz; *m*-Ph), 112.3 (s; ReC≡*C*), 105.8 (d, *J*(C, P) = 15.9 Hz; Re*C*≡C), 100.6 (s; $C_5(CH_3)_5$), 93.5 (d, *J*(C, P) = 2.7 Hz; *C*≡CSi), 80.6 (s; C≡*C*Si), 10.0 (s; $C_5(CH_3)_5$), 0.91 (s; $Si(CH_3)_3$); $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 25 °C, 85% H_3PO_4 ext.): δ = 21.1 (s); IR (CH_2Cl_2/KBr): $\tilde{\nu}$ = 2118/2119(m), 2098/2097(m) (C≡C), 1653/1648(s) cm⁻¹ (NO); MS (EI, 30 eV): *m*/*z* (%) 735 (100) [M^+]. Correct elemental analysis.

4: Orange solid; m.p. 84–86 °C (decomp.); ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = 7.75–7.65 (m, 6H, $3C_6H_5$), 7.07–6.94 (m, 9H; $3C_6H_5$), 1.95 (d, *J*(H, P) = 1.0 Hz, 1H; ≡CH) 1.57 (s, 15H; $C_5(CH_3)_5$); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C, C_6D_6 int.): δ = 135.4 (d, *J*(C, P) = 51.4 Hz; *i*-Ph), 134.3 (d, *J*(C, P) = 10.9 Hz; *o*-Ph), 130.2 (s; *p*-Ph), 128.3 (d, *J*(C, P) = 10.0 Hz; *m*-Ph), 110.8 (s; ReC≡C), 102.1 (d, *J*(C, P) = 15.9 Hz; Re*C*≡C), 100.5 (s; $C_5(CH_3)_5$), 72.4 (s; *C*≡CH), 65.2 (s; C≡*C*H), 10.0 (s; $C_5(CH_3)_5$); $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 25 °C, 85% H_3PO_4 ext.): δ = 20.9 (s); IR (CH_2Cl_2/KBr): $\tilde{\nu}$ = 3305/3287(m) (≡C-H), 2115/2113(s), 1975/1975(w) (C≡C), 1644/1645(s) cm⁻¹ (NO); MS (EI, 70 eV): *m*/*z*(%) 663(4) [M^+]. Correct elemental analysis.

5: Yellow-orange solid, m.p. 61–65 °C (decomp.); ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = 7.80–7.72 (m, 6H; $3C_6H_5$), 7.07–6.92 (m, 9H; $3C_6H_5$), 1.81 (s, 3H; $\equiv CCH_3$), 1.61 (s, 15H; $C_5(CH_3)_5$); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C, C_6D_6 int.): δ = 135.7 (d, *J*(C, P) = 50.6 Hz; *i*-Ph), 134.4 (d, *J*(C, P) = 10.2 Hz; *o*-Ph), 130.1 (s; *p*-Ph), 128.3 (d, *J*(C, P) = 9.8 Hz; *m*-Ph), 111.6 (s, ReC≡*C*), 100.3 (s; $C_5(CH_3)_5$), 96.8 (d, *J*(C, P) = 17.3 Hz; Re*C*≡C), 71.9 (s; $C{\equiv}CCH_3$), 69.1 (d, *J*(C, P) = 3.1 Hz; $C{\equiv}CCH_3$), 10.0 (s; $C_5(CH_3)_5$, 4.5 (s; $\equiv CCH_3$); $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 25 °C, 85% H_3PO_4 ext.): δ = 21.0 (s); IR (CH_2Cl_2/KBr): $\tilde{\nu}$ = 2193/2194(m), 2027/2029(m) (C≡C), 1644/1644(s) cm⁻¹ (NO); MS (EI, 70 eV): *m*/*z* (%) 677 (100) [M^+].

8 and **9**: see Experimental Procedure.

10: Yellow-brown solid, m.p. 101–106 °C (decomp.); ^1H NMR (300 MHz, CD_2Cl_2, 25 °C, CD_2Cl_2 int.): δ = 7.57–7.46 (m, 15H; $3C_6H_5$), 1.93 (s, 15H; $C_5(CH_3)_5$); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C, C_6D_6 int.): δ = 287.8 (s; Mn=C), 221.1 (d, *J*(C, P) = 11.8 Hz; Re*C*C), 218.2 (s; CO), 218.0 (s; CO), 168.9 (s; ReC*C*), 133.5 (d, *J*(C, P) = 11.3 Hz; *o*-Ph), 132.6 (s; *p*-Ph), 129.7 (d, *J*(C, P) = 11.1 Hz; *m*-Ph), 108.0 (s; $C_5(CH_3)_5$) 100.1 (s; C_5Cl_5), 10.1 (s; $C_5(CH_3)_5$); $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 25 °C, 85% H_3PO_4 ext.): δ = 19.7 (s); IR (CH_2Cl_2): $\tilde{\nu}$ = 1899(vs) (C=C=C), 2047(m), 2007(w) (C≡O), 1717(s) cm⁻¹ (NO); UV/VIS (CH_2Cl_2): λ_{max} (ε) = 266 sh (17000), 334 sh (16000), 414 (49000), 554 sh nm (2700); MS (positive ions FAB (Cs^+), 3-NBA/benzene matrix): *m*/*z* (%) 998(30) [M^+], 615 (100) [$\{Re^*\}^+ + 1$]. Correct elemental analysis.

Complex **4** was treated with 1.0 equiv of *n*BuLi in THF at −80 °C. When the reaction was monitored by ^{31}P NMR, resonances were observed at δ = 21.3 and 21.0 (70:30; **4**, δ = 21.0). One sharp resonance was obtained when the sample was warmed to 10–20 °C (δ = 21.0). Addition of MeI, either at −80 °C or room temperature, gave the 1,3-pentadiynyl complex **5** (δ = 20.9) in 95% yield, as determined by NMR and IR spectroscopy.[8] These data were taken as evidence for the formation of C_4Li complex **6**, which is possibly present as a mixture of aggregates. The deprotonation of a butadiynyl iron complex and subsequent reactions with metal halides to give $[L_nMC{\equiv}C{-}C{\equiv}CM'L'_n]$ complexes has been previously reported by Wong.[9]

We sought to elaborate **6** to a bimetallic Fischer carbene complex. Thus, $[(\eta^5\text{-}C_5H_5)Mn(CO)_3]$ and $[Me_3O]^+[BF_4]^-$ were added to **6** under various conditions; however, no evidence was found for an adduct with a $ReC{\equiv}C{-}C{\equiv}CC(OMe){=}Mn$ linkage, although the corresponding reaction of the lower homologue **7** worked well.[2] The major product was **5**. Hence, an analogous

$[\{Re^*\}(C{\equiv}CLi)]$ **7**, $\{Re^*\} = (\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)$

reaction was conducted with $(\eta^5\text{-}C_5Cl_5)Mn(CO)_3$,[10] which should be more conducive to nucleophile addition from the standpoints of both reaction rate and equilibrium. Workup gave the dark purple C_5OMe complex **8** (77% yield).[11] Thus, the $ReC{\equiv}C{-}C{\equiv}CLi$ moiety in **6** is less basic and/or nucleophilic than the $ReC{\equiv}CLi$ moiety in **7**, a trend often observed for organic analogues.

Toluene/hexane solutions of **8** were treated with excess BF_3 gas (Scheme 1). The C_5 complex **9** precipitated as a dark brown solid. Workup gave **9** (52% yield) that was approximately 94% pure by NMR spectroscopy. Several unusual properties of **9** became immediately apparent and have so far precluded further purification or crystallization. First, **9** is extremely light-sensitive, both in solution and the solid state. Second, **9** decomposes on the time scale of hours in the dark at room temperature; the rate apparently depends upon the concentration of **9**. In all cases, a black decomposition product formed that gave ESR signals and broad NMR signals.[12] Elemental analyses gave values for the carbon, hydrogen, and chlorine content that were within 1–5% of those calculated for **9**.

Complex **9** was characterized spectroscopically. The ^{13}C NMR spectrum showed a downfield ReC signal ($\delta = 218.4$) with a $^2J(C, P)$ value (12.5 Hz) near the range typical of $^+Re{=}C$ linkages (10.0–12.3 Hz) and smaller than that characteristic of $Re{-}C{\equiv}$ linkages (15.8–17.3 Hz).[13] Other signals assigned to the C_5 chain were observed at $\delta = 296.2$ (MnC), 119.1, 110.6, and 107.0. The $\tilde{\nu}(NO)$ value ($1718\ cm^{-1}$) in the IR spectrum was in a range diagnostic of cationic $^+Re{=}C$ compounds ($1719-1698\ cm^{-1}$) and much higher than that characteristic of neutral $Re{-}C{\equiv}C$ compounds ($1653-1630\ cm^{-1}$). Thus, the cumulene resonance form $^+Re{=}C{=}C{=}C{=}C{=}C{=}Mn$ dominates over the alternative $Re{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}Mn^+$ (Scheme 1).[15] A very strong IR band at $1953\ cm^{-1}$ was presumed to be associated with the cumulene fragment.

We sought to characterize the optical properties of **9**. As a prelude, the new C_3 complex **10** was prepared similarly to **9** from $ReC{\equiv}CLi$ complex **7**. Complex **10**, and the previously reported chlorine-free analogue **11**, did not exhibit any unusual photochemical or thermal reactivity.[2] Thus, the cyclopentadienyl chlorines in **9** are not an intrinsic source of instability. This implicates the carbon chain length in **11** as the key labilizing feature. Complex **10** exhibited signals in the IR ($\tilde{\nu} = 1717$(s) (NO), 1899(vs) cm^{-1} ($C{=}C{=}C$)) and ^{13}C NMR ($\delta = 221.1$ (d, $^2J(C, P) = 11.8$ Hz; ReC), 287.8 (s; MnC), 168.9 (s; CCC)) spectra indicative of a dominant "cumulenic" resonance form, $^+Re{=}C{=}C{=}C{=}Mn$. These results parallel those for **11**, which was also crystallographically characterized.[2]

$[\{Re^*\}(CCC)Mn(CO)_2(\eta^5\text{-}C_5Cl_5)]^+\ [BF_4]^-$ **10**
$[\{Re^*\}(CCC)Mn(CO)_2(\eta^5\text{-}C_5H_5)]^+\ [BF_4]^-$ **11**

The UV/visible spectra of **9–11** are compared in Figure 1. The yellow-brown solutions show very intense absorptions at 480 (**9**), 414 (**10**), and 392 (**11**) nm (ε = 60500, 49000, and 56000 $M^{-1}cm^{-1}$, respectively). Weaker bands occur at longer wavelengths (634, 554 sh, and 484 nm; ε = 4800, 2700, and 3700 $M^{-1}cm^{-1}$). Thus, either increased carbon chain lengths (**9** vs **10**) or electronegative chlorine substituents on the manganese cyclopentadienyl ligand (**10** vs **11**) result in absorptions at longer wavelengths. The latter trend suggests that the transitions have appreciable rhenium-to-manganese charge transfer character.

Attempts to trap **9** as a stable adduct have to date been unsuccessful. No reaction occurs with TCNE, ethylene, or SMe_2 at ambient temperature, and PMe_3 gives a complex mixture of unusual products. Nonetheless, we anticipate an array of unusual properties for this series of compounds. Further examples of complexes with C_5 and longer chains will be reported in the near future.

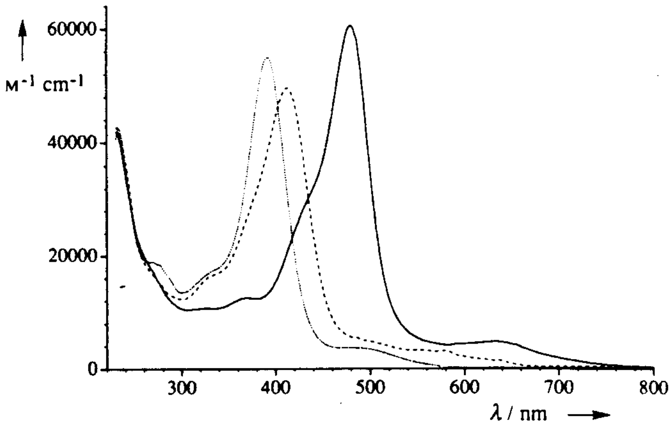


Fig. 1. UV/visible spectra of compounds **9–11**. (CH_2Cl_2, ambient temperature, $c = 2.3-3.9\times10^{-5}$ M). — **9**, ---- **10**, · · · · **11**.

Experimental Procedure

8: A Schlenk tube was charged with **4** (0.048 g, 0.072 mmol) in THF (5 mL). The mixture was cooled to −80 °C. Then *n*BuLi (36 µL, 2.3 M in hexane) was added with stirring. After 1 h, a solution of $[(\eta^5\text{-}C_5Cl_5)Mn(CO)_3]$ [10] (0.028 g, 0.075 mmol) in THF (3 mL) was added via a cannula. After 1 h, the cold bath was removed. After a further hour, the red-orange solution was transferred via a cannula to a Schlenk flask that had been charged with $[Me_3O]^+[BF_4]^-$ (0.050 g, 0.32 mmol). The mixture was cooled to −80 °C and stirred for 0.5 h. The cold bath was then removed. After 0.5 h, the sample was concentrated to ca. 2 mL, and hexane (10 mL) was added. Chromatography (N_2, Florisil; hexane → hexane/THF 1/1 (v/v)) gave a deep purple fraction. The solvent was removed under oil pump vacuum to give **8** as a dark purple powder (0.059 g, 0.056 mmol, 77%). M.p. 114–116 °C; ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = 7.65–7.55 (m, 6H; $3C_6H_5$), 7.12–6.95 (m, 9H; $3C_6H_5$), 3.53 (s, 3H; OCH_3), 1.55 (s, 15H; $C_5(CH_3)_5$); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C, C_6D_6 int.): δ = 288.9 (s; Mn=C), 228.2 (s; CO), 228.1 (s; CO), 167.1 (d, $J(C, P)$ = 14.8 Hz; $Re\mathit{C}{\equiv}C$), 134.2 (d, $J(C, P)$ = 52.4 Hz; *i*-Ph), 134.0 (d, $J(C, P)$ = 10.8 Hz; *o*-Ph), 130.7 (s; *p*-Ph), 128.6 (d, $J(C, P)$ = 10.3 Hz; *m*-Ph), 127.4, 116.3, 82.4 (3s; $C{\equiv}\mathit{CC}{\equiv}\mathit{C}C{=}$), 102.1 (s; $\mathit{C}_5(CH_3)_5$), 97.0 (s; C_5Cl_5), 63.3 (s; OCH_3), 9.9 (s; $C_5(\mathit{C}H_3)_5$); $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 25 °C, 85% H_3PO_4 ext.): δ = 20.6 (s); IR (CH_2Cl_2/KBr): $\tilde{\nu}$ = 2057/2054(m), 2046/2044(m) sh ($C{\equiv}C$), 1965/1962(s), 1925/1922(s) ($C{\equiv}O$), 1655/1657(s) cm^{-1} (NO); UV/VIS (CH_2Cl_2): λ_{max} (ε) = 264 sh (29000), 318 (19000), 376 sh (13000), 502 sh (14500,) 562 nm (21000); MS (positive ions FAB (Cs^+), 3-NBA/benzene matrix): *m/z* (%) 1053 (3) [M^+], 614 (100) [$\{Re\}^+$]. Correct elemental analysis.

9: This procedure was carried out in the dark. A Schlenk tube was charged with **8** (0.094 g, 0.089 mmol), toluene (10 mL), and hexane (8 mL). The mixture was cooled to −60 °C. Then BF_3 gas was bubbled through the solution for 1 min. A dark solid precipitated. The supernatant was removed with a syringe, and the solid was washed with hexane (3 × 5 mL) and dried under oil pump vacuum. The solid was extracted with CH_2Cl_2 (2 × 2 mL). The extracts were filtered through a Celite pad (1 cm). Hexane (10 mL) was added, and the dark brown precipitate was collected by filtration, washed with hexane (2 × 2 mL), and dried under oil pump vacuum to give **9** (0.051 g, 0.046 mmol, 52%). ^1H NMR (300 MHz, CD_2Cl_2, 25 °C, CD_2Cl_2 int): δ = 7.64–7.49 (m, 9H; $3C_6H_5$), 7.48–7.36 (m, 6H; $3C_6H_5$), 1.95 (s, 15H; $C_5(CH_3)_5$); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, −20 °C, CD_2Cl_2 int.): δ = 296.2 (s; MnC), 220.8 (s; CO), 220.2 (s; CO), 218.4 (d, $J(C, P)$ = 12.5 Hz; ReC), 133.2 (d, $J(C, P)$ = 10.9 Hz; *o*-Ph), 132.4 (s; *p*-Ph), 129.5 (d, $J(C, P)$ = 10.6 Hz; *m*-Ph), 119.1, 110.6, 107.0 (3s; $C\mathit{CCC}C$), 108.5 (s; $\mathit{C}_5(CH_3)_5$), 100.4 (s; C_5Cl_5), 10.0 (s; $C_5(\mathit{C}H_3)_5$); $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 85% H_3PO_4 ext.): δ = 20.5 (s); IR (CH_2Cl_2/KBr): $\tilde{\nu}$ = 2045/2042(s), 2008/1996(s) ($C{\equiv}0$), 1953/1948(vs) ($C{=}C{=}C{=}C{=}C$), 1718/1705(s) cm^{-1} (NO); UV/VIS (CH_2Cl_2): λ_{max} (ε) = 262 (19000), 370 (12500), 442 sh (33000), 480 (60000), 634 nm (4800); MS (positive ions FAB (Cs^+), 3-NBA/CH_2Cl_2 matrix): *m/z* (%): 1022 (4) [M^+], 614 (100) [$\{Re\}^+$].

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[11] Analogous reactions with the monochlorocyclopentadienyl complex $[(\eta^5\text{-}C_5H_4Cl)Mn(CO)_3]$ gave mixtures of **5** and a C_5OMe adduct that we could not easily purify.

[12] Isolated by precipitation with hexane or ether. Found (two independently prepared samples): C, 44.77–42.64; H, 3.54–3.17; Cl, 12.51–12.41. Calcd for precursor **9**: C, 43.33; H, 2.73; Cl, 15.99. A UV visible spectrum showed no features at > 300 nm other than intense tailing. A FAB mass spectrum showed no peaks with *m/z* higher than 614 ([{Re*}$^+$]). IR (CH_2Cl_2): $\tilde{\nu}$ = 1726(s) br, 2043(s), 1974(s), and weaker unresolved bands at 1850–2000 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2, 25 °C, CD_2Cl_2 int.): δ = 7.75 (br m; C_6H_5), 1.95 (s; $C_5(CH_3)_5$); ^{31}P NMR (121 MHz, CD_2Cl_2, 25 °C, 85% H_3PO_4 ext.): δ = 22 (br s); ESR (CH_2Cl_2) (*g*) 2.02 (sextet, A_{iso} 97 G).

[13] Limiting values are taken from **3–5** and pentamethylcyclopentadienyl complexes in ref. [4a] and [8].

[14] The ^{13}C NMR chemical shifts of the ReC and CMn units are also consistent with this conclusion, although the former is intermediate between limiting model compounds, and the latter must be compared with neutral carbene and cationic carbyne complexes of the $[(\eta^5\text{-}C_5H_5)Mn(CO)_2]$ fragment [2].

A Novel Hexamer of Bu*t*C≡P: Synthesis, Structure, and Theoretical Studies**

Vinicius Caliman, Peter B. Hitchcock, John F. Nixon,* Matthias Hofmann, and Paul von Ragué Schleyer*

The organic and organometallic chemistry of phosphaalkynes (RC≡P) is developing rapidly.[1–4] The very recent report[5] by de Meijere and co-workers of the "cage" hydrocarbon $C_{12}H_{12}$ (**1**), with D_{3d} symmetry, prompts us to describe the synthesis and structure of the novel isostructural $P_6C_6tBu_6$ cage compound (**2**) that represents the largest known oligomer of the phosphaalkyne *t*BuC≡P.

A landmark in the chemistry of phosphaalkynes was Regitz et al.'s synthesis and structural characterization of the very stable tetraphosphacubane $P_4C_4tBu_4$ (**3**), made either thermally from *t*BuC≡P or more efficiently by use of the precursor complex $[Zr(\eta^5\text{-}C_5H_5)_2(P_2C_2tBu_2)]$.[6, 7] Previously[8] the related pentameric cage compound $P_5C_5tBu_5$ (**4**) was obtained readily by oxidative coupling of the 1,3-di- and 1,2,4-triphosphacyclopentadienyl ring systems **5** and **6**. The structure of pentamer **4** is closely related to that of the tetraphosphacubane, **3** as one corner C atom of the "cube" can be considered to be replaced by a triangle of CCP atoms (Fig. 1).

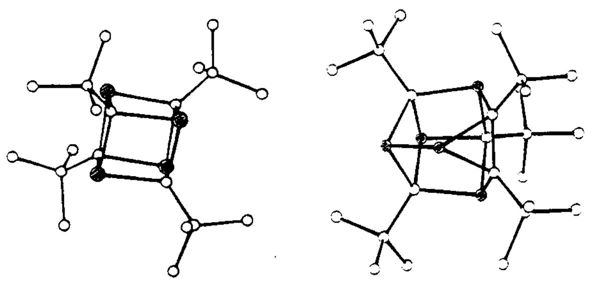

Fig. 1. Structure of **3** (left) and **4** (right) in the crystal. (○ carbon, ● phosphorus) [6–8].

Whereas the $P_3C_2tBu_2^-$ ring ion exhibits η^1- and η^5-ligating behavior towards transition metals, the corresponding $P_2C_3tBu_3^-$ ion only exhibited η^5- or η^3-ligation.[1, 9, 10] Since the structurally well characterized $\eta^1\text{-}P_3C_2tBu_2$ complexes typified by $[M(\eta^1\text{-}P_3C_2tBu_2)_x(PR_3)_yX_z]$ (M = Pd, Pt; X = halide; $x = 2, y = 2, z = 0$; $x = 1, y = 2, z = 1$) all contained stabilizing phosphane ligands,[11] we have now carried out a reaction of the more labile complex $[PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene) with a mixture of the $P_3C_2tBu_2^-$ and $P_2C_3tBu_3^-$ ring ions in dimethoxyethane and obtained nonmetal-containing organophosphorus compounds, presumably via unstable organometallic intermediates.

The reaction product mixture was chromatographed and the known $P_5C_5tBu_5$ (**4**), $P_5C_5tBu_5H_2$ (**7**), and the new compound $P_4C_6tBu_6H_2$ (**8**), whose structure is similar to **7**, were separated and characterized by their $^{31}P\{^1H\}$ NMR spectra.[8, 12, 13] Of special interest was a fraction which yielded a colorless compound (**2**), which exhibited a parent ion in the mass spectrum at *m/e* = 600, indicative of a hexamer of *t*BuCP. The $^{31}P\{^1H\}$ NMR spectrum of **2** is very simple, consisting of two singlets of relative intensity 2:1 whose chemical shifts are characteristic of $\lambda^3\sigma^3$ P atoms (δ = 4.8 (P^A), 184.0 (P^B); relative to H_3PO_4). The simplicity of the ^1H NMR spectrum (singlets at δ = 1.64 and 1.25 of relative intensity 1:2) strongly suggests a highly symmetric cage structure.

The molecular structure of $P_6C_6tBu_6$ (**2**), which was established subsequently by a single crystal X-ray structural determination,[14] consists of a lanternlike hexameric cage containing two 3-membered CCP rings (Fig. 2). There is a close similarity between the C_{2h} symmetry exhibited by **2** and the D_{3d} symmetry of the $C_{12}H_{12}$ hydrocarbon p-[$3^2.5^6$]-octahedrane (**1**, Fig. 3, left),[5] as well as the obvious structural relationship of **2** to the D_{3d} structure computed recently for the hypothetical P_{12} molecule **9**[15] (Fig. 3, right). These results provide further strong support for previous contentions about the similarity in chemical behavior of P and CR fragments in both organic and organometallic chemistry.[1, 2, 3]

Ab initio calculations on oligomers of HCP as a model for *t*BuCP oligomers were performed with the Gaussian 92 program.[19] The MP2(fu)/6-21G* (fu = full, all electrons correlated) geometry of the model hexamer is in good accord with that determined for **2**. Experimental bond lengths and bond angles for $P_6C_6tBu_6$ and corresponding theoretical values for $P_6C_6H_6$ are summarized in Figure 4. Reaction energies computed at different levels for the HCP → 1/*n*(HCP)*n* (*n* = 2–6) reac-

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