New Families of Coordinated Carbon: Oxidative Coupling of an Ethynyl Complex to Isolable and Crystallographically Characterized MC≡CC≡CM and $^+$M=C=C=C=C=M$^+$ Assemblies

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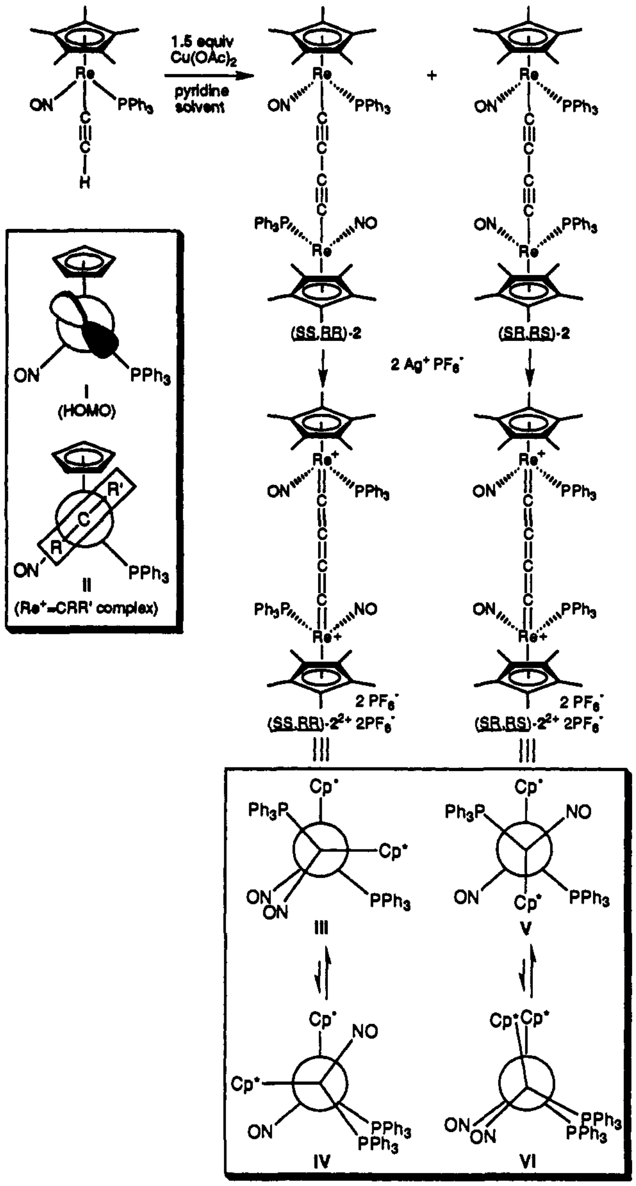
There is rapidly growing interest in the chemical, physical, and materials properties of compounds in which linear elemental carbon chains (C_x) span two transition metals, $L_nMC_xM'L'_{n'}$.[1-4] Two classes of complexes offer particularly exciting frontiers for synthesis and study: (1) those with higher carbon chains ($\geq C_3$)[3,4] and (2) those that differ only in the oxidation state of the MC_xM' linkage.[4g] Toward these ends, we have sought to develop approaches to C_x complexes involving ethynyl complexes, $L_nMC{\equiv}CH$.[2,3] Specifically, we wondered whether it would be possible to effect oxidative couplings to μ-η^1:η^1-butadiynyl C_4 complexes, $L_nMC{\equiv}CC{\equiv}CML_n$, analogously to well-known reactions of organic terminal alkynes. Although there is only scant precedent for coupling -C≡H units in metal coordination spheres,[5] such processes offer tantalizing potential for the synthesis of unusual dimeric, oligomeric, and polymeric species.[6]

Thus, the chiral, racemic rhenium ethynyl complex (η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CH) (**1**)[7] and $Cu(OAc)_2$ (1.5 equiv) were reacted in pyridine. Workup gave the air-stable, orange-brown ReC_4Re complex (η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC≡C)(Ph_3P)(ON)Re(η^5-C_5Me_5) (**2**) in 88% yield as a 50:50 diastereomer mixture (Scheme I). Crystallization from dichloromethane/ether gave the diastereomerically pure solvate (*SS*,*RR*)-**2**·2CH_2Cl_2, which was characterized by microanalysis and NMR ($^1H/^{13}C/^{31}P$) and IR spectroscopy.[8] The stereochemistry was assigned crystallographically (below). Isotopically labeled (*SS*,*RR*)-**2**-$^{13}C_4$ was similarly prepared and gave $^{13}C\{^1H\}$ NMR peaks (ppm, C_6D_6) at 95.8 (C_α, ddd, $J_{CP}/J_{CC}/J_{CC}$ 10.9/96.5/47.1 Hz) and 117.5 (C_β, dd, J_{CC} 97.2/47.6 Hz). IR spectra showed $\nu_{C\equiv C}$, $\nu_{^{13}C\equiv ^{13}C}$, and ν_{NO} absorptions at (cm^{-1}, CH_2Cl_2) 1964 (w), 1888 (w; calcd 1887), and 1623 (s), respectively. Samples enriched in the opposite (meso) diastereomer, (*SR*,*RS*)-**2**, were recovered from crystallizations.[8]

Scheme I. Synthesis of Neutral and Dicationic ReC_4Re Complexes



Many cationic rhenium alkylidene and vinylidene complexes of the formula [(η^5-C_5R_5)Re(NO)(PPh_3)(=C_x=CRR')]$^+X^-$ (**3**; x = 0,1) have been isolated previously.[7,9] Thus, the *di*cation of **2**, which can be formulated with a $^+$Re=C=C=C=C=Re$^+$ linkage, was viewed as a viable synthetic target. Guided by cyclic voltammetry data given elsewhere,[10] we oxidized (*SS*,*RR*)-**2** with $Ag^+PF_6^-$ (2.5 equiv; Scheme I). Workup afforded the air-stable, deep-blue butatrienediylidene complex (*SS*,*RR*)-**2**$^{2+}$·2PF_6^- (86%), which was characterized analogously to (*SS*,*RR*)-**2**.[8] A $^{13}C\{^1H\}$ NMR spectrum of the similarly prepared $^{13}C_4$ derivative gave a characteristic downfield Re=C_α resonance (ppm, CD_2Cl_2) at

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(1) (a) Diederich, F.; Rubin, Y. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1101. (b) For lead references to compound with C_1 and C_2 chains, see the preceding papers in this series.[2,3]

(2) Ramsden, J. A.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5890.

(3) $L_nMCCCM'L'_{n'}$ complexes: Weng, W.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 3824.

(4) $L_nMCCCCM'L'_{n'}$ complexes: (a) Sonogashira, K.; Kataoka, S.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *160*, 319. (b) Wong, A.; Kang, P. C. W.; Tagge, C. D.; Leon, D. R. *Organometallics* **1990**, *9*, 1992. (c) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188. (d) Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1992**, *114*, 4411. (e) Crescenzi, R.; Sterzo, C. L. *Organometallics* **1992**, *11*, 4301. (f) Rappert, T.; Nürnberg, O.; Werner, H. *Ibid.* **1993**, *12*, 1359. (g) Le Narvor, N.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 357. (h) **Note Added in Proof**: The crystal structure of a RuC≡CC≡CRu complex has been reported: Bruce, M. I.; Hinterding, P.; Tiekink, E. R. T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1993**, *450*, 209.

(5) (a) Ferrocene derivatives: Schlögl, K.; Steyrer, W. *J. Organomet. Chem.* **1966**, *6*, 399 and references therein. (b) Preliminary data for ethynyl complexes: Kim, P. J.; Masai, H.; Sonogashira, K.; Hagihara, N. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 181. (c) Polymerizations of *trans*-$(R_3P)_2$Pt-(C≡CC≡CH)$_2$ and related compounds: Takahashi, S.; Murata, S.; Sonogashira, K.; Hagihara, N. *J. Polym. Sci.* **1980**, *18*, 661. (d) Cyclooligomerization of a dicobalt 1,3,5-hexatriyne complex: Rubin, Y.; Knobler, C.; Diederich, F. *J. Am. Chem. Soc.* **1990**, *112*, 4966. (e) See also: Iyer, R. S.; Selegue, J. P. *Ibid.* **1987**, *109*, 910. Bitcon, C.; Whiteley, M. W. *J. Organomet. Chem.* **1987**, *336*, 385.

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(7) Ramsden, J. A.; Weng, W.; Gladysz, J. A. *Organometallics* **1992**, *11*, 3635.

(8) Complete spectroscopic and analytical data are given in the supplementary material. Mass spectra did not show any higher C_x^+ ions.

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305.1 (ddd, $J_{CP}/J_{CC}/J_{CC}$ 12.3/77.0/40.7 Hz) and a C_β resonance at 213.5 (dd, J_{CC} 77.0/40.7 Hz). The IR ν_{NO} value (1719 cm^{-1} s, CH_2Cl_2) was much greater than that of **2**, consistent with reduced back-bonding, but no cumulenic $\nu(C_x)$ bands were observed. Samples enriched in the opposite diastereomer, (*SR,RS*)-$\mathbf{2}^{2+}\cdot 2PF_6^-$, were also prepared.[8]

Further support was sought for the cumulenic electronic structure of $\mathbf{2}^{2+}\cdot 2PF_6^-$. Importantly, alkylidene and vinylidene complexes **3** have previously been shown to exist as geometric isomers that differ in the orientation of the =CRR′ termini and interconvert with barriers of 18–21 kcal/mol.[7,9] Crystal structures establish Re=C conformations that allow high degrees of overlap of the C_α p acceptor orbitals and the rhenium fragment HOMO shown in **I**, as illustrated for alkylidene complexes in **II** (Scheme I). Hence, (*SS,RR*)- and (*SR,RS*)-$\mathbf{2}^{2+}\cdot 2PF_6^-$ should give geometric isomers with the idealized structures **III**/**IV** and **V**/**VI**, respectively. Accordingly, ^{31}P NMR spectra in CD_2Cl_2 at −93 °C showed *two* resonances for each diastereomer (*SS,RR*, 26.8/28.4 ppm, 62:38; *SR,RS*, 26.1/28.2 ppm, 89:11).[11] The major and minor *SS,RR* isomers are tentatively assigned to **III** and **IV**, in which the bulky PPh_3 ligands are *anti* and *syn*. The major and minor *SR,RS* isomers are undoubtedly **V** (staggered, no *syn* ligands) and **VI** (eclipsed, three *syn* ligands). These would logically have a greater free energy difference than **III** and **IV**, as reflected by the relative isomer ratios.

No C_4 complexes (or pairs of C_x complexes in different oxidation states) have been structurally characterized to date.[4h] Thus, crystal structures of (*SS,RR*)-$\mathbf{2}\cdot 2CH_2Cl_2$ and (*SS,RR*)-$\mathbf{2}^{2+}\cdot 2PF_6^-$ were determined (Figure 1). Both compounds have nearly linear ReC_4Re units, with bond angles of 170–177°. The former exhibits C≡C and C—C bond lengths (1.202(7)/1.389(5) Å) very close to those in butadiyne (1.218(2)/1.384(2) Å)[12] and a Re—C bond length (2.037(5) Å) similar to those of related Re—C≡C—Pd and Re—C≡C—CH_3 compounds (2.079(9), 2.066(7) Å).[2] The dication exhibits C_α=C_β and C_β=$C_{\beta'}$ bond lengths (1.24(2)/1.26(2), 1.33(2) Å) near those of butatriene (1.284(6)–1.309(3) Å) or hexapentenes (1.267–1.332 Å)[13,14] and Re=C bond lengths (1.93(1)/1.91(1) Å) close to those in alkylidene (1.949(6)–1.945(4) Å) and vinylidene (1.84(2) Å) complexes **3**.[9]

The Re–Re distances in (*SS,RR*)-$\mathbf{2}\cdot 2CH_2Cl_2$ and (*SS,RR*)-$\mathbf{2}^{2+}\cdot 2PF_6^-$ are 7.8288(4) and 7.6350(8) Å. The contraction upon oxidation is consistent with the increase in ReC_4Re linkage π bonds from four to five and occurs despite the potential for electrostatic repulsion. The angle of the P–Re–C_α planes about the stereoelectronically unconstrained C_4 bridge in (*SS,RR*)-$\mathbf{2}\cdot 2CH_2Cl_2$ is 148°, giving a roughly *anti* arrangement of the bulky PPh_3 ligands. However, the corresponding angle in (*SS,RR*)-$\mathbf{2}^{2+}\cdot 2PF_6^-$ is 23°, which places the PPh_3 ligands *syn*, as in the idealized isomer **IV** (Scheme I). Thus, the less stable geometric isomer preferentially crystallizes.

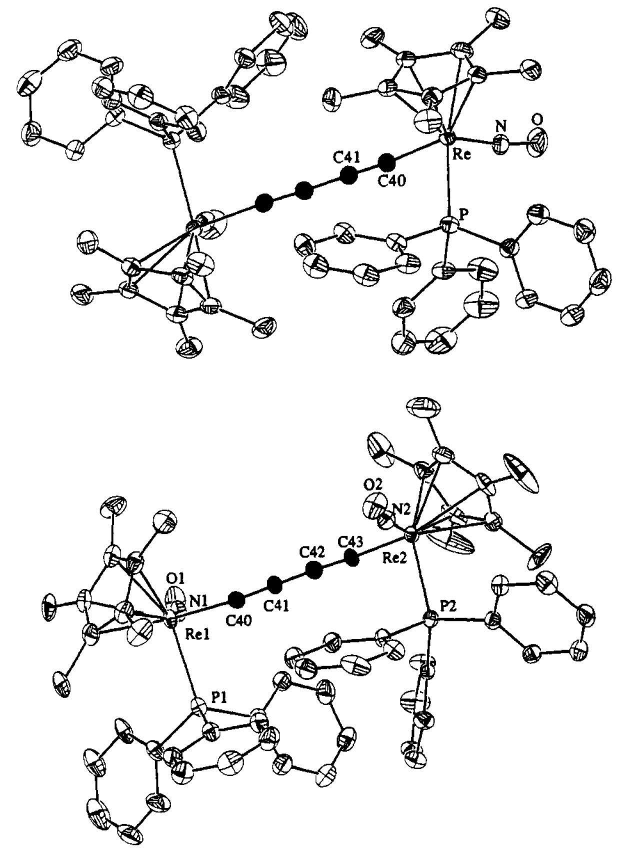

Figure 1. Structures of (*SS,RR*)-$\mathbf{2}\cdot 2CH_2Cl_2$ (top) and the dication of (*SS,RR*)-$\mathbf{2}^{2+}\cdot 2PF_6^-$ (bottom). Key bond lengths (Å) and angles (deg): (*SS,RR*)-$\mathbf{2}\cdot 2CH_2Cl_2$, Re–C40 2.037(5), C40–C41 1.202(7), C41–C41′ 1.389(5), Re–P 2.375(1), Re–N 1.754(5), Re–C40–C41 174.4(5), C40–C41–C41′ 176.8(6); (*SS,RR*)-$\mathbf{2}^{2+}\cdot 2PF_6^-$, Re1–C40 1.93(1), C40–C41 1.24(2), C41–C42 1.33(2), C42–C43 1.26(2), Re2–C43 1.91(1), Re1–P1 2.438(4), Re2–P2 2.431(4), Re1–N1 1.77(1), Re2–N2 1.78(1), Re1–C40–C41 170(1), C40–C41–C42 177(2), C41–C42–C43 177(2), Re2–C42–C43 174(1).

While this work was in progress, Lapinte reported the synthesis of related iron C_4 complexes of the formula $[(\eta^5\text{-}C_5Me_5)Fe(dppe)(CCCC)(dppe)Fe(\eta^5\text{-}C_5Me_5)]^{n+}\cdot nX^-$.[4g] These important and complementary results provide further evidence for the ready accessibility of multiple redox states in $L_nMC_xM'L'_{n'}$ compounds. Extensions of the preparative methodology developed above to other C_x complexes and the isolation of a related radical cation with unusual spectroscopic properties will be described in the near future.[10]

Acknowledgment. We thank the NSF for support of this research.

Supplementary Material Available: Characterization of **2** and $\mathbf{2}^{2+}\cdot 2PF_6^-$; tables of crystallographic data for (*SS,RR*)-$\mathbf{2}\cdot 2CH_2Cl_2$ and (*SS,RR*)-$\mathbf{2}^{2+}\cdot 2PF_6^-$ (14 pages); listing of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

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(11) When samples are warmed, the ^{31}P resonances markedly shift and broaden. Only one peak is observed above −22 °C (*SS,RR*) and −5 °C (*SR,RS*). However, we are not yet certain whether genuine coalescences have occurred. These equilibria cannot be probed by ^1H or ^{13}C NMR, as the stereocenters are remote and the chemical shift differences are too small.

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(14) Interestingly, the C=C bond length pattern appears to be opposite that in butatrienes (C_α=C_β > C_β=$C_{\beta'}$) but analogous to that in hexapentenes (C_β=C_γ < C_γ=$C_{\gamma'}$).[13] The latter may be better structural models, as the numbers of π bonds and sp-hydridized carbons are identical with those of $\mathbf{2}^{2+}\cdot 2PF_6^-$.