Organometallics **1994,** *13,* 4159−4161

Methylene Complexes of Higher Nuclearity Clusters: $[PPN][Re_7C(CO)_{21}(\mu\text{-}CH_2)]$ and $[PPN]_2[Re_6C(CO)_{18}(\mu\text{-}CH_2)]$

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Received July 26, 1994[⊗]

Summary: Oxidation of $[PPN]_3[Re_7C(CO)_{21}]$ *with ferrocenium (2 equiv) followed by the addition of diazomethane has provided* $[PPN][Re_7C(CO)_{21}(\mu\text{-}CH_2)]$ *in 74% isolated yield. The structure of the compound, which is the first reported example of a methylene ligand in a higher nuclearity cluster, has been defined by single-crystal X-ray diffraction. A second methylene derivative,* $[PPN]_2[Re_6C(CO)_{18}(\mu\text{-}CH_2)]$*, is formed (>70%) by "decapping" the first compound with acetonitrile in the presence of* PPN^+.

The controlled synthesis of derivatives of higher nuclearity metal carbonyl clusters is in a stage of early development.[1,2] A particularly promising method for relatively robust anionic clusters is "oxidative substitution," viz., two-electron oxidation coupled with addition of an electron pair donor.[2−6] In particular, $[Re_7C(CO)_{21}]^{3-}$ has been found to react with either carbon monoxide or triphenyl phosphite upon oxidation to give $[Re_7C(CO)_{22}]^{-}$[5] or $[Re_7C(CO)_{21}P(OPh)_3]^{-}$,[6] respectively. We report here that an oxidative substitution reaction of $[Re_7C(CO)_{21}]^{3-}$ with diazomethane provides $[Re_7C(CO)_{21}(\mu\text{-}CH_2)]^{-}$ *and* that "decapping" the latter compound provides also $[Re_6C(CO)_{18}(\mu\text{-}CH_2)]^{2-}$. These compounds are the first reported examples of a methylene ligand bound to a higher nuclearity cluster framework.

Treatment of $[Re_7C(CO)_{21}]^{3-}$ with 2 equiv of ferrocenium ion in dichloromethane formed a green-black solution, which showed a strong IR band at 2016 cm^{-1}, presumably due to $[Re_7C(CO)_{21}]^{-}$.[7] Addition of diazomethane caused a color change to red, and $[Re_7C(CO)_{21}(\mu\text{-}CH_2]^{-}$ was subsequently isolated as the PPN^+ salt in 74% yield.[8] An analogous reaction conducted with (trimethylsilyl)diazomethane gave a black solid that proved to be a mixture (by ^1H NMR and FAB-MS)[9] of the expected $[Re_7C(CO)_{21}(\mu\text{-}CH\text{-}TMS)]^{-}$ and $[Re_7C(CO)_{21}(\mu\text{-}CH_2)]^{-}$ (TMS = trimethylsilyl). The latter is apparently formed by facile protodesilylation.

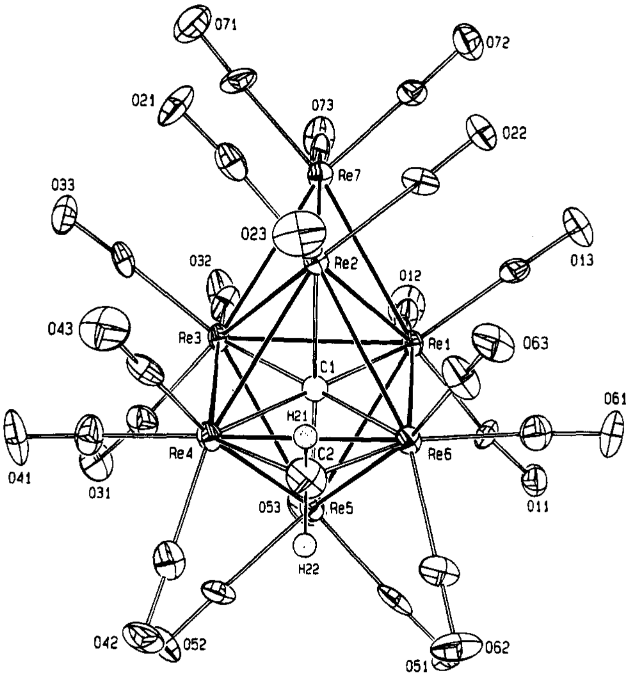

Figure 1. ORTEP diagram of the cluster anion in $[PPN][Re_7C(CO)_{21}(\mu\text{-}CH_2)]$. Hydrogen atoms shown on methylene carbon C(2) are in calculated positions. Selected bond distances (Å): Re(1)−Re(2) = 2.9430(8); Re(1)−Re(3) = 2.9752(8); Re(1)−Re(5) = 2.9516(9); Re(1)−Re(6) = 3.0409(8); Re(1)−Re(7) = 2.9941(9); Re(2)−Re(3) = 2.9358(7); Re(2)−Re(4) = 3.0309(9); Re(2)−Re(6) = 2.9860(9); Re(2)−Re(7) = 2.9401(8); Re(3)−Re(4) = 3.0042(8); Re(3)−Re(5) = 2.9682(9); Re(3)−Re(7) = 2.9746(9); Re(4)−Re(5) = 3.0376(9); Re(4)−Re(6) = 2.9089(8); Re(5)−Re(6) = 3.0583(9); Re(4)−C(2) = 2.24(2); Re(6)−C(2) = 2.20(2); Re−C(1) = 2.11(2) (average).

A structural diagram of the cluster anion $[Re_7C(CO)_{21}(\mu\text{-}CH_2)]^{-}$ is shown in Figure 1.[10] The molecule is composed of an octahedral $Re_6(\mu_6\text{-}C)(CO)_{18}$ core (with three carbonyl ligands per rhenium atom) capped on one triangular face by an additional $Re(CO)_3$ moiety. The rhenium−rhenium and rhenium−carbide distances are in accord with those of related heptanuclear rhenium cluster compounds.[5,6] The methylene ligand is in a bridging position between two rhenium atoms associated with the triangular face opposite the capping Re-

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[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1994.

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(7) One equivalent of $[Cp_2Fe]^+$ generates the radical species $[Re_7C(CO)_{21}]^{2-}$,[5] which shows ν_{CO} at 1991 cm^{-1}. The degree of oxidation of $[Re_7C(CO)_{21}]^{3-}$ is also affected by ion pairing: Hsu, G.; Shapley, J. R. Unpublished observations.

(8) A dichloromethane solution of $[PPN]_3[Re_7C(CO)_{21}]$ (159 mg, 0.0452 mmol) was treated with $[Cp_2Fe][PF_6]$ (36 mg, 0,.11 mmol) and then dropwise with ethereal diazomethane until a clear, red solution formed. The residue, after solvent removal, was crystallized from dichloromethane/cyclohexane by solvent diffusion to give $[PPN][Re_7C(CO)_{21}(CH_2)]$ (82 mg, 0.033 mmol, 74%). Anal. Calcd for $C_{59}H_{32}NO_{21}P_2Re_7$: C, 28.85; H, 1.31; N, 0.57. Found: C, 28.83; H, 1.36; N, 0.58. Negative-ion FAB mass spectrum (^{187}Re): *m/z* 1923 ($Re_7C(CO)_{21}(CH_2)$), 1895 ($Re_7C(CO)_{21}(CH_2)$ − CO), 1867 ($Re_7C(CO)_{21}(CH_2)$ − 2CO). IR (acetone): ν_{CO} 2076 (vw), 2028 (s), 2017 (vs), 2005 (w, sh), 1953 (w, sh), 1938 (w, sh), 1921 (w, sh), 1905 (w) cm^{-1}. ^1H NMR (300 MHz, acetone-d_6, 20 °C): δ 9.03 (d, 1 H), 8.49 (d, 1 H, J = 7.8 Hz), 8.0−7.45 (m, 30 H, C_6H_5 in PPN^+). $[PPN][Re_7{}^{13}C({}^{13}CO)_{21}(CH_2)]$ was prepared from $[PPN]_3[Re_7{}^{13}C({}^{13}CO)_{21}]$ (ca. 30% ^{13}C). ^{13}C NMR (75 MHz, acetone-d_6, 20 °C): δ 200.2 (s, 3 C), 194.6 (s, 3 C), 189 br, 6 C), 188.3 (s, 3 C), 186−183 (br, 6 C).

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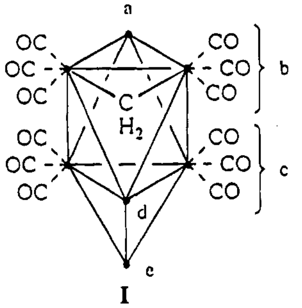
$(CO)_3$ group. The dihedral angle formed by the methylene carbon with respect to the Re(4)–Re(6)–Re(2) face is 116.8(7)°, whereas the corresponding angle formed with the Re(4)–Re(6)–Re(5) face is 137.5(7)°.

The general location of the methylene ligand in $[Re_7C(CO)_{21}(\mu\text{-}CH_2)]^-$ is the same as that of the bridging carbonyl ligand in $[Re_7C(CO)_{21}(\mu\text{-}CO)]^-$.[5] The rhenium–carbon distances for the methylene ligand (Re–C(2) = 2.22(2) Å (average)) are also quite comparable with those observed for the bridging carbonyl ligand (2.19(1) Å). Similar distances have been determined for the methylene ligands in the trinuclear clusters $(\mu\text{-}H)_2Os_3(CO)_{10}(\mu\text{-}CH_2)$ (2.151(5), 2.150(6) Å)[11] and $Os_3(CO)_9(C_2Ph_2)(\mu\text{-}CH_2)$ (2.16(2), 2.19(2) Å).[12] The metal–metal distance (Re(4)–Re(6) = 2.9089(8) Å) associated with the edge bridged by the methylene ligand is significantly shorter than the other rhenium–rhenium distances. This feature is not found in $[Re_7C(CO)_{21}(\mu\text{-}CO)]^-$.[5] Theoretical analysis has indicated that a bridging methylene ligand is both a better σ-donor and a better π-acceptor than a bridging carbonyl ligand.[13] Thus, a stronger bonding interaction is expected with a methylene bridge than with a carbonyl bridge when analogous metal centers are involved.

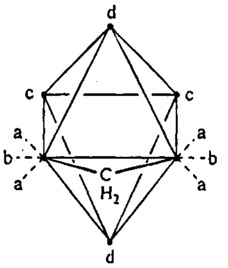
The ^1H NMR parameters for the inequivalent methylene protons in $[Re_7C(CO)_{21}(\mu\text{-}CH_2)]^-$ (δ 9.03, 8.49; J_{H-H} = 7.8 Hz) are quite comparable with those reported for other μ-methylene compounds,[14] in particular the triosmium clusters $(\mu\text{-}H)_2Os_3(CO)_{10}(\mu\text{-}CH_2)$ (δ 5.12, 4.32; J_{H-H} = 5.9 Hz),[15] $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ (δ 7.83, 6.68; J_{H-H} = 6.9 Hz),[16] and $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)(\mu\text{-}CH_2)$ (δ 8.75, 7.65; J_{H-H} = 5 Hz).[12] The carbonyl region ^{13}C NMR spectra of $[PPN][Re_7C(^{13}CO)_{21}(\mu\text{-}CH_2)]$ are entirely consistent with the solid-state structure (see I). At 20 °C three sharp signals at δ 200.2 (3C) (*e*), 194.6 (3C) (*d*), and 188.3 (3C) (*a*) and two broad resonances at δ 189.1 (6C) (*c*) and at ca. 185 (6C) (*b*) were observed. At −60 °C, one broad signal (*c*) was split into a set of three resonances (*c′*) at δ 190.1 (2C), 188.1 (2C), and 186.5 (2C), and the other broad signal (*b*) was a set of three resonances (*b′*) at δ 185.4 (2C), and 183.6 (2C). The sharp signal at lowest field corresponds to the carbonyl ligands bonded to the capping rhenium atom (*e*).[6] The specific assignments of sets *d* and *a* are not individually definitive but correspond to previous assignments for $[Re_7C(CO)_{22}]^-$.[6] The carbonyls flanking the bridging methylene (set *b*) clearly have a significant barrier to local 3-fold rotation, and internuclear steric interactions with set *c* may increase its barrier as well.



I

Treatment of $[Re_7C(CO)_{21}(\mu\text{-}CH_2)]^-$ with acetonitrile provided $[Re_6C(CO)_{18}(\mu\text{-}CH_2)]^{2-}$, which was isolated as the PPN$^+$ salt in 70% yield.[17] This transformation paralleled other observations of decapping reactions with heptarhenium compounds, viz., that $[Re_7C(CO)_{22}]^-$ was decapped by triphenylphosphine or acetonitrile to give $[Re_6C(CO)_{19}]^{2-}$,[18,19] that $[Re_7C(CO)_{21}(P(OPh)_3)]^-$ was decapped by acetonitrile also to give $[Re_6C(CO)_{19}]^{2-}$,[6] and that $[H_2Re_7C(CO)_{21}]^-$ analogously generated $[H_2Re_6C(CO)_{18}]^{2-}$.[20] In the case of $[Re_7C(CO)_{21}(P(OPh)_3)]$; the phosphite ligand was bonded to the rhenium cap that was removed;[6] in the other cases the $Re(CO)_3$ cap was selectively removed in acetonitrile as $[Re(CO)_3(NCCH_3)_3]^+$. An alternative route to $[Re_6C(CO)_{18}(\mu\text{-}CH_2)]^{2-}$ is via photolysis of $[Re_6C(CO)_{19}]^{2-}$,[18] followed by treatment with diazomethane, but the isolated yield was significantly lower.

The variable-temperature ^{13}C NMR spectra (carbonyl region) of $[PPN]_2[Re_6{}^{13}C(^{13}CO)_{18}(\mu\text{-}CH_2)]$ showed four carbonyl resonances at −80 °C. Two sharp signals at δ 199.7 (6C) and 198.7 (6C) are assigned to the two sets of carbonyl ligands (*c*,*d*) bonded to the rhenium atoms adjacent to each of the rhenium atoms supporting the methylene ligand (see II). The signal at δ 192.0 (2C) is attributed to the two equivalent carbonyl ligands in the plane formed by the methylene carbon and the two rhenium atoms bonded to it (*b*), and the signal at δ 191.7 (4C) is attributed to the equivalent carbonyl ligands on either side of this plane (*a*). At room temperature these last two signals coalesced into one, apparently due to local 3-fold rotation.



II

Both $[Re_7C(CO)_{21}(\mu\text{-}CO)]^-$ and $[Re_6C(CO)_{18}(\mu\text{-}CO)]^{2-}$ show facile and complete internuclear carbonyl scram-

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(9) Data attributed to $[Re_7C(CO)_{21}(\mu\text{-}CH\text{-}TMS)]^-$ include the following: ^1H NMR (acetone-d_6, 20 °C δ 10.45 (s) and 9.48 (s), two isomers, equal intensity; negative ion FAB-MS (^{187}Re) m/z 1995 ($Re_7C(CO)_{21}(CH\text{-}TMS)$), 1967 (M − CO), 1724 (M − $Re(CO)_3$).

(10) Crystals of $[PPN][Re_7C(CO)_{21}(CH_2)]$ suitable for diffraction studies were grown by vapor diffusion of pentane into a dichloromethane solution. Crystal data: triclinic, space group $P\bar{1}$, with a = 12.295(4) Å, b = 14.958(8) Å, c = 16.617(6) Å, α = 90.20(4)°, β = 96.15(3)°, γ = 91.71(4)°, and Z = 2 (at T = −75 °C). Data collection was carried out at −75 °C on an Enraf-Nonius CAD4 automated κ-axis diffractometer. A total of 9491 independent reflections, 7194 observed with $I > 2.58\sigma(I)$, in the range $2° < 2\theta < 48°$ were measured at variable rates over a period of 104 h with no change in the appearance of the sample. Data were corrected numerically for absorption (μ(Mo Kα) = 142.13 cm^{-1}) and for anomalous dispersion, Lorentz, and polarization effects. The structure was solved by direct methods (SHELXS-86); correct positions for the metal atoms were deduced from an *E*-map. Subsequent least-squares refinement and difference Fourier syntheses (SHELX-76) revealed positions for the remaining non-hydrogen atoms. Final agreement factors were R = 0.051 and R_w = 0.063.

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bling.[6,18] Both of these compounds also possess an "extra" CO ligand, i.e., one CO beyond the count of 3 CO/Re center. Distortions induced by the extra carbonyl in the overall carbonyl ligand coordination shell of the clusters presumably lower the barriers to internuclear carbonyl migration. In the present cases the extra ligand is a bridging methylene, which does not move as easily to a terminal site[21] and therefore expectedly inhibits carbonyl scrambling at the supporting rhenium centers. Surprisingly, however, the presence of the methylene ligand also "freezes" internuclear carbonyl mobility at more remote sites, e.g., the capping $Re(CO)_3$ group in $[Re_7C(CO)_{21}(\mu\text{-}CH_2)]^-$ (vide supra). Understanding the balance between local and global effects of substitution is a prime point of attention in ongoing studies of these compounds.

Acknowledgment. This research was supported by National Science Foundation Grant CHE 89-15349.

Supplementary Material Available: Tables of crystallographic data, atom coordinates, thermal coefficients, bond distances, and bond angles from the structure determination of $[PPN][Re_7C(CO)_2(\mu\text{-}CH_2)]$ (6 pages). Ordering information is given on any current masthead page.

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(17) $[PPN][Re_7C(CO)_{21}(CH_2)]$ (30 mg, 0.012 mmol) was dissolved in acetonitrile (30 mL), and the solution was stirred under a nitrogen atmosphere for 3 h. The IR bands for $[Re(CO)_3(NCCH_3)_3]^+$ at 2054 and 1953 cm^{-1} became prominent. [PPN]Cl (0.1 g) was added, and the solution was concentrated to 3 mL. Crystallization was induced by adding a layer of 2-propanol, giving red crystals of $[PPN]_2[Re_6C(CO)_{18}(CH_2)]$ (24 mg, 0.0086 mmol, 70%). Anal. Calcd for $C_{92}H_{62}N_2O_{18}P_4Re_6$: C, 40.56; H, 2.29; N, 1.03. Found: C, 40.62; H, 2.64; N, 1.00. IR (acetone): ν_{CO} 2077 (vw), 2045 (vw), 1991 (s), 1987 (s, sh), 1977 (vs), 1903 (m) cm^{-1}. ^1H NMR (300 MHz, acetone-d_6, 20 °C): δ 7.9−7.5 (m, 60 H, C_6H_5 in PPN$^+$), 7.42 (s, 2 H). Negative-ion FAB mass spectrum (^{187}Re): *m/z* 1652 ($Re_6C(CO)_{18}(CH_2)$), 1624 ($Re_6C(CO)_{18}(CH_2) - CO$). $[PPN]_2[Re_6{}^{13}C(^{13}CO)_{18}(CH_2)]$ was made analogously from $[PPN]_3[Re_7{}^{13}C(^{13}CO)_{21}]$ (ca. 30% ^{13}C). ^{13}C NMR (75 MHz, acetone-d_6, 0 °C): δ 422.5 (s, 1 C, μ_6-C), 199.7 (s, 6 C), 198.7 (s, 6 C), 193.3 (m, 6 C). ^{13}C NMR (75 Hz, dichloromethane-d_2 −80 °C): δ 198.7 (s, 6 C), 197.6 (s, 6 C), 192.0 (s, 2 C), 191.7 (s, 4 C).

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