Reaction of 1 with CNC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_3$. To a suspension of 0.52 g (1.03 mmol) of **1** in 30 mL of toluene was added 0.38 mL (2.16 mmol) of 1,1,3,3-tetramethylbutyl isocyanide (**2c**) at room temperature with stirring. After 1 h, a clear yellow solution was obtained, which was concentrated to 15 mL and cooled to -30 °C to give 0.65 g (82%) of **3c** as slightly yellow needles, mp 160 °C (DTA) dec. Anal. Calcd for $C_{40}H_{58}N_2O_2Zr_2$ (781.4): C, 61.49; H, 7.48; N, 3.59. Found: C, 61.78; H, 7.56; N, 3.60. IR (KBr): ν(C=N) 1621 cm^{-1}. MS (70 eV, EI): *m/z* = 778 (1%, M$^+$), 500 (3), 470 (35), 390 (15), 220 (16), 57 (100). ^{1}H NMR (benzene-d_6, 200 MHz): δ 5.86 (s, 20 H, Cp), 5.02 (s, 4 H, ZrOCH$_2$), 1.83 (s, 4 H, CCH$_2$C), 1.29 (s, 12 H, C(CH$_3$)$_2$), 1.26 (s, 18 H, C(CH$_3$)$_3$). ^{13}C NMR (benzene-d_6, 50 MHz): δ 215.9 (C=N), 110.3 ($^1J_{CH}$ = 172 Hz, Cp), 85.1 ($^1J_{CH}$ = 139 Hz, ZrOCH$_2$), 64.2 (NCMe$_2$), 57.8 ($^1J_{CH}$ = 124 Hz, CCH$_2$C), 32.4 (CMe$_3$), 32.4 ($^1J_{CH}$ = 125 Hz, C(CH$_3$)$_2$), 30.2 ($^1J_{CH}$ = 124 Hz, C(CH$_3$)$_3$).

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Registry No. 1, 88385-20-0; **2a**, 30718-17-3; **2b**, 72443-18-6; **2c**, 14542-93-9; **3a**, 132776-60-4; **3b**, 132776-62-6; **3c**, 132776-61-5.

Supplementary Material Available: For **3a**, tables of detailed information on the crystal structure determination, final atomic position parameters, final thermal parameters, and interatomic distances and angles (7 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

Synthesis of Alkoxymethyl Complexes from Metal Formyls

Dorothy H. Gibson,* Kathryn Owens, Santosh K. Mandal, William E. Sattich, and
Jaime O. Franco

Department of Chemistry, University of Louisville, Louisville, Kentucky 40292

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Summary: Syntheses of seven alkoxymethyl complexes, M-CH$_2$OR (R = Me, Et), from the corresponding metal formyls are described; the metals are manganese (compounds **1a-b**, **2**, and **3**), rhenium (compounds **4** and **5**), or molybdenum (compound **6**). Four of these (**1b** and **3-5**) are new compounds; the details of the syntheses of the other three have not been reported previously. Examples are given of three distinct synthetic routes; all routes require initiation by the action of an electrophile on the metal formyl complex. Variations in the procedures are dictated by the reactivity of the formyl complex and that of its protonated or alkylated form.

Alkoxymethyl complexes are useful precursors to carbene complexes[1] and several other types of C$_1$ ligands to transition metals.[2] A variety of methods have been reported for their synthesis: (1) by reaction of a metal anion with a halomethyl ether,[3] (2) by nucleophilic substitution on a halomethyl complex by an alcohol or an alkoxide,[4] (3) by reduction of a secondary alkoxycarbene complex,[5] (4) by alkylation of a cationic η^2-formaldehyde complex,[6] (5) by oxidative addition of a halomethyl ether to a coordinatively unsaturated complex,[7] (6) by hydride abstraction from a methyl complex followed by alkoxide addition,[8] (7) by decarbonylation of an alkoxyacetyl complex,[9] (8) by reduction of a metal carbonyl cation in the presence of an alcohol,[10] and (9) by reaction of a hydroxymethyl complex with an alcohol.[11] In addition to method 1, several others depend, indirectly, on the availability of a metal anion. Methods 1 and 2 are the ones which have been most commonly used. Although effective, method 1 is objectionable because of the toxicity of halomethyl ethers.

Table I. Summary of Synthetic Methods for Alkoxymethyl Complexes

compd	synth method	prod yield, %^{a}/reacn time
cis-Mn(CO)$_4$PPh$_3$(CH$_2$OCH$_3$) (**1a**)	A	84/15 min
cis-Mn(CO)$_4$PPh$_3$(CH$_2$OCH$_2$CH$_3$) (**1b**)	A	68/15 min
mer,trans-Mn(CO)$_3$(PPh$_3$)$_2$(CH$_2$OCH$_3$) (**2**)	B	78/14 h
same	C	86^b/10 min
mer,trans-Mn(CO)$_3$[P(OPh)$_3$]$_2$(CH$_2$OCH$_3$) (**3**)	B	80/3 h
mer,trans-Re(CO)$_3$(PPh$_3$)$_2$(CH$_2$OCH$_3$) (**4**)	C	89/20 min
same	C	86^b/15 min
mer,trans-Re(CO)$_3$[P(OPh)$_3$]$_2$(CH$_2$OCH$_3$) (**5**)	B	61/30 min
cis- and *trans*-CpMo(CO)$_2$[P(OPh$_3$)]CH$_2$OCH$_3$ (**6**)	A	63/5 min

^{a} Product yields are based on reaction stoichiometry. ^{b} The isolated carbene complex was used; the overall time and yield from the formyl complex are reported.

The present work includes method 3 but details examples of three distinct routes to alkoxymethyl complexes from neutral metal formyl complexes. All three routes utilize an electrophile to initiate further transformation of the formyl complex;[12] the choice of method is dictated by the reactivity of the substrate and that of its protonated

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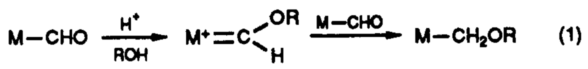
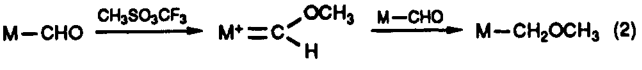
or alkylated form. The three routes utilizing reactions of formyl complexes are identified as

method A:



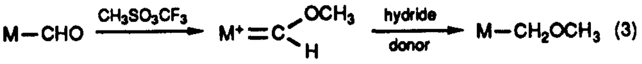
$$M{-}CHO \xrightarrow[ROH]{H^+} M^+{=}C\begin{smallmatrix}OR\\H\end{smallmatrix} \xrightarrow{M-CHO} M{-}CH_2OR \qquad (1)$$

method B:



$$M{-}CHO \xrightarrow{CH_3SO_3CF_3} M^+{=}C\begin{smallmatrix}OCH_3\\H\end{smallmatrix} \xrightarrow{M-CHO} M{-}CH_2OCH_3 \qquad (2)$$

method C:



$$M{-}CHO \xrightarrow{CH_3SO_3CF_3} M^+{=}C\begin{smallmatrix}OCH_3\\H\end{smallmatrix} \xrightarrow[donor]{hydride} M{-}CH_2OCH_3 \qquad (3)$$

involves reaction with a protonic acid in the presence of an alcohol, method B involves reaction with an alkylating agent, and method C involves reaction with an alkylating agent followed by an independent reducing agent. Seven alkoxymethyl complexes have been prepared and are identified in Table I, which also summarizes the synthetic procedures.

The intermediacy of a carbene complex in each case is supported by the isolation of several of the hydroxy- or methoxycarbene complexes from related reactions[13] and by the previous observations of others.[14] It appears that the electrophilic characteristics of the intermediate carbene complex in reactions of this type will determine whether excess formyl complex will suffice as the hydride donor or whether a more active reagent will be required to accomplish the last step. Comparison of the syntheses of compounds **1a** and **2** (by the first procedure) is useful in this regard. In both cases the formyl complex is used as the hydride donor, but the synthesis of **1a** is complete after 15 min while the preparation of **2** requires 14 h. For electronic reasons, the bis(phosphine)-substituted formyl complex should be the better hydride donor; also, the steric environment for hydride donation should be little worse than in the bis(phosphite) analogue. Yet, compound **3** was formed much more readily than **2** by the same synthetic method.

Four of the complexes (**1b** and **3**–**5**) are new; the other three have been reported previously, but the full details of their syntheses were not described. Thus, **1a** and **2** were made previously by ligand substitution[15] of $Mn(CO)_5(CH_2OCH_3)$, but the procedure for the synthesis of this parent compound was not reported. Ligand substitution leading to **1a** gave a 74% yield from the parent compound, but the bis(phosphine) complex **2** was obtained in only 26% yield by this method. The spectral characteristics of **6** have been reported, but the details of its synthesis have not.[16]

The spectral properties of **1a**, **2**, and **6** are in agreement with those reported previously. The other compounds have been characterized by elemental analyses and by IR and by ^1H and ^{13}C NMR spectral data. Compound **1b** shows the same four-band pattern in the carbonyl stretching region of its IR spectrum as **1a**; this pattern is characteristic of cis-disubstituted octahedral complexes.[17] Also, the ^{13}C NMR spectrum of each compound shows three doublets for the carbonyl carbons, as expected. The carbonyl stretching frequencies of **3**–**5** show the same three-band pattern (weak, strong, and medium intensities) as compound **2** and that is characteristic of *mer,trans*-trisubstituted octahedral complexes.[18] Furthermore, the ^{13}C NMR spectrum of each compound shows the terminal carbonyl resonances as two triplets (with intensity ratios of 2:1), as expected.

In the cases where the formyl complex has been used as the hydride donor, the corresponding metal carbonyl cation is the other reaction product. This product can be easily recovered and reused in the synthesis of additional formyl complex.

For the reactions which are initiated by a protonic acid, as outlined in eq 1, there are two stages at which the initial electrophile might be replaced by an alkyl group from an alcohol: (a) with $M(=CHOH)^+$ or (b) with $M(CH_2{-}OH)$. There are several instances in which a hydroxymethyl complex has been converted to an alkoxymethyl complex by the action of an alcohol,[10,11] but we can find no previous report of a similar reaction with a hydroxycarbene complex. However, treatment of $Mn(CO)_3(PPh_3)(=CHOH)^+CH_3C_6H_4SO_3^-$ with methanol does convert it to the known[13b] methoxycarbene complex: thus solvolysis of an intermediate carbene cation represents a viable step on the path to the final alkoxymethyl complex.

Experimental Section

General Data. All reactions were carried out under an atmosphere of prepurified nitrogen. Reagent grade dichloromethane and anhydrous ether were used as received. Reagent grade methanol, ethanol, and 2-propanol were dried over 3-Å molecular sieves and distilled. Reagent grade hexane and benzene were dried over concentrated sulfuric acid and fractionally distilled. Spectroscopic measurements were obtained on the following instruments: ^1H NMR, Varian XL-300, EM-390, and T-60; ^{13}C NMR, Varian XL-300; IR, Perkin-Elmer 599B. NMR chemical shifts are referenced to TMS. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Methyl triflate (Aldrich), *p*-toluenesulfonic acid monohydrate (Aldrich), and sodium borohydride (Aldrich) were used as received. The formyl complexes, *cis*-$Mn(CO)_4(PPh_3)CHO$, *mer,trans*-$Mn(CO)_3(PPh_3)_2CHO$, *mer,trans*-$Mn(CO)_3[P(OPh)_3]_2CHO$, *mer,trans*-$Re(CO)_3(PPh_3)_2CHO$, *mer,trans*-$Re(CO)_3[P(OPh)_3]_2CHO$, and $CpMo(CO)_2[P(OPh)_3]CHO$ were synthesized from previously published methods,[12] as were the carbene complexes[13] *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHOCH_3)^+CF_3SO_3^-$, *mer,trans*-$Re(CO)_3(PPh_3)_2(CHOCH_3)^+CF_3SO_3^-$, and *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHOH)^+CH_3C_6H_4SO_3^-$.

Preparation of *cis*-$Mn(CO)_4(PPh_3)(CH_2OCH_3)$ (1a). To 20 mL of methanol containing *p*-toluenesulfonic acid monohydrate (0.322 g, 1.69 mmol) and chilled to 0 °C was added *cis*-$Mn(CO)_4(PPh_3)CHO$ (0.46 g, 0.84 mmol) with stirring. After 15 min, the solvent was removed on a rotary evaporator. The pale yellow residue was triturated with 3 × 10 mL of hexane; the combined hexane extracts were filtered, and the filtrate was concentrated and then chilled to −20 °C. The resulting precipitate was collected to give 0.19 g (84%) of **1a** as pale yellow microcrystals. IR (hexane): ν_{CO} 2060 (m), 1987 (s), 1960 (vs) 1937 (s) cm^{-1} [lit.[15a] IR (CH_2Cl_2): ν_{CO} 2062 (m), 1982 (sh), 1967 (vs), 1936 (s) cm^{-1}]. ^1H NMR (acetone-d_6): δ 7.60 (m), 3.66 (d, J_{PH} = 7.0 Hz), 3.05 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 218.9 (d, J_{PC} = 6.8 Hz), 218.5 (d, J_{PC} = 22.0 Hz), 215.9 (d, J_{PC} = 15.0 Hz), 133.9 (d, J_{PC} = 40.1 Hz), 133.5 (d, J_{PC} = 10.0 Hz), 130.7 (s), 128.9 (d, J_{PC} = 9.5 Hz), 71.2 (d, J_{PC} = 11.5 Hz), 63.6 (s) [lit.[15a] ^1H NMR (CD_2Cl_2): δ 7.45 (m), 3.43 (d, J_{PH} = 6.8 Hz), 3.07 (s)]. The insoluble residue was dissolved in CH_2Cl_2 (10 mL) and extracted with 3 × 10 mL of water; the CH_2Cl_2 layer was dried over $MgSO_4$ and mixed with

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ether (10 mL), and the mixture was cooled to −20 °C to effect crystallization. The off-white solid was collected by filtration and dried, giving 0.260 g (82%) of $Mn(CO)_5(PPh_3)^+OTs^-$ as an off-white powder. IR (CH_2Cl_2): ν_{CO} 2140 (m), 2070 (sh), 2050 (vs) cm^{-1} [lit.[12] for $Mn(CO)_5(PPh_3)^+BF_4^-$: same].

Preparation of *cis*-$Mn(CO)_4(PPh_3)(CH_2OCH_2CH_3)$ (1b). To 20 mL of ethanol containing *p*-toluenesulfonic acid monohydrate (0.415 g, 2.18 mmol) and maintained at 0 °C was added *cis*-$Mn(CO)_4(PPh_3)CHO$ (0.500 g, 1.09 mmol) with stirring. After 15 min, the solvent was removed on a rotary evaporator. The pale yellow residue was triturated with 3 × 10 mL of hexane; the combined extracts were washed with 3 × 30 mL of water, dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure and then chilled to −20 °C to precipitate 0.185 g (68% yield) of **1b** as pale yellow microcrystals; mp 78–79 °C. Anal. Calcd for $C_{25}H_{22}O_5PMn$: C, 61.35; H, 4.53; P, 6.33. Found: C, 61.51; H, 4.68; P, 6.52. IR (hexane): ν_{CO} 2060 (m), 1987 (s), 1960 (vs), 1936 (s) cm^{-1}. ^1H NMR (acetone-d_6): δ 7.40 (m), 3.65 (d, J_{PH} = 7.0 Hz), 3.12 (q, J_{HH} = 7.0 Hz), 1.02 (t, J_{HH} = 7.0 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 218.6 (d, J_{PC} = 9.8 Hz), 218.4 (d, J_{PC} = 22.0 Hz), 215.6 (d, J_{PC} = 15.6 Hz), 133.0 (d, J_{PC} = 9.5 Hz), 132.8 (d, J_{PC} = 40.5 Hz), 130.0 (s), 128.3 (d, J_{PC} = 9.8 Hz), 71.1 (s), 67.9 (d, J_{PC} = 11.5 Hz), 15.0 (s). The insoluble portion was dissolved in CH_2Cl_2 (10 mL), extracted with 3 × 10 mL of water, dried over anhydrous $MgSO_4$, and filtered. Ether (10 mL) was added to the filtrate and the mixture cooled to −20 °C to precipitate $Mn(CO)_5(PPh_3)^+OTs^-$ (0.277 g, 81% yield); the product had the same IR spectral properties reported above.

Preparation of *mer,trans*-$Mn(CO)_3(PPh_3)_2(CH_2OCH_3)$ (2). Method 1. By Reaction of *mer,trans*-$Mn(CO)_3(PPh_3)_2CHO$ with $CH_3SO_3CF_3$. To a CH_2Cl_2 solution (20 mL) containing $CH_3SO_3CF_3$ (0.118 g, 0.72 mmol) at −78 °C was added *mer,-trans*-$Mn(CO)_3(PPh_3)_2CHO$ (0.500 g, 0.72 mmol) with stirring; the reaction was complete in 5 min. Then *mer,trans*-$Mn(CO)_3(PPh_3)_2CHO$ (0.500 g, 0.72 mmol) was added, and this mixture was allowed to warm slowly to room temperature and stirred overnight (14 h). Solvent was removed under reduced pressure, and the residue was triturated with benzene (20 mL); the benzene extract was filtered and then concentrated to 10 mL. After mixing with hexane (10 mL), it was cooled to −5 °C to give the pale yellow needle-shaped crystals of **2** (0.40 g, 78% yield). IR (CH_2Cl_2): ν_{CO} 2004 (w), 1915 (s), 1879 (m) cm^{-1} [lit.[15a] IR (CH_2Cl_2): ν_{CO} 2010 (w), 1921 (s), 1885 (m) cm^{-1}]. ^1H NMR (CD_2Cl_2): δ 7.47 (m), 3.05 (t, J_{PH} = 7.5 Hz), 2.43 (s) [lit.[15a] ^1H NMR ($CDCl_3$): δ 7.52 (m), 3.13 (t, J_{PH} = 7.5 Hz), 2.52 (s)]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 224.0 (t, J_{PC} = 21.8 Hz), 222.5 (t, J_{PC} = 18.0 Hz), 136.5 (m), 133.6 (t, J_{PC} = 4.8 Hz), 129.7 (s), 128.3 (t, J_{PC} = 5.1 Hz), 75.3 (t, J_{PC} = 13.6 Hz), 63.5 (s). The benzene-insoluble residue from above was dissolved in CH_2Cl_2 (5 mL), the solution was mixed with hexane (10 mL), and the resulting mixture was chilled at −20 °C to precipitate *trans*-$Mn(CO)_4(PPh_3)_2^+CF_3SO_3^-$ (0.453 g, 75 %) as a yellow powder. IR (CH_2Cl_2): ν_{CO} 2040 (w), 2000 (vs) cm^{-1} [lit.[12] for *trans*-$Mn(CO)_4(PPh_3)_2^+BF_4^-$ IR (CH_2Cl_2): ν_{CO} 2090 (vw), 2040 (w), 1996 (vs) cm^{-1}].

Method 2. By Reaction of *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHOCH_3)^+CF_3SO_3^-$ with Sodium Borohydride. To a CH_2Cl_2 solution (25 mL) containing *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHOCH_3)^+CF_3SO_3^-$ (0.500 g, 0.58 mmol) at 0 °C were added $NaBH_4$ (0.044 g, 1.16 mmol) and methanol (10 mL) with stirring. After 5 min, the mixture was warmed to room temperature and the solvent was removed under reduced pressure giving a pale yellow residue. The residue was dissolved in benzene (15 mL) and extracted with water. The benzene solution was dried over anhydrous $MgSO_4$ and filtered; the filtrate was mixed with hexane (15 mL), and the mixture was cooled to −5 °C. Yellow crystals were formed (0.316 g, 88% yield); the spectral characteristics of this product were the same as those described above.

Preparation of *mer,trans*-$Mn(CO)_3[P(OPh)_3]_2(CH_2OCH_3)$ (3). In a 50-mL Schlenk vessel, *mer,trans*-$Mn(CO)_3[P(OPh)_3]_2CHO$ (1.00 g, 1.3 mmol) was stirred at 0 °C in 15 mL of CH_2Cl_2. $CF_3SO_3CH_3$ (0.090 mL, 0.79 mmol) in 3 mL of CH_2Cl_2 was added dropwise over the course of 2 h. The mixture was allowed to stir for 1 h; then the mixture was allowed to warm to room temperature and filtered through a glass pad. Solvent was removed from the filtrate under vacuum, and the residue was triturated with 3 × 15 mL of ether. The ether extracts were evaporated to dryness, and the residue was recrystallized from CH_2Cl_2/pentane to give pale yellow needles (0.40 g, 80% yield); mp 112–114 °C. Anal. Calcd for $C_{41}H_{35}O_{10}P_2Mn$: C, 61.20; H, 4.38; P, 7.70. Found: C, 60.87; H, 4.50; P, 7.56. IR (CH_2Cl_2): ν_{CO} 2040 (vw), 1958 (vs), 1935 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.24 (m), 4.01 (t, J_{PH} = 8.1 Hz), 3.16 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 218.0 (t, J_{PC} = 33.3 Hz), 215.5 (t, J_{PC} = 21.0 Hz), 152.0 (t, J_{PC} = 5.1 Hz), 129.9 (s), 125.0 (s), 121.4 (s), 68.5 (t, J_{PC} = 20.8 Hz), 64.1 (s). The ether-insoluble portion of the reaction was recrystallized in CH_2Cl_2 to yield white needles of *trans*-$Mn(CO)_4[P(OPh)_3]_2^+CF_3SO_3^-$ (0.54 g, 92% yield). IR (CH_2Cl_2): ν_{CO} 2115 (vw), 2070 (w), 2040 (s) cm^{-1} [lit.[12] for *trans*-$Mn(CO)_4[P(OPh)_3]_2^+BF_4^-$: same].

Preparation of *mer,trans*-$Re(CO)_3(PPh_3)_2(CH_2OCH_3)$ (4). Method 1. From *mer,trans*-$Re(CO)_3(PPh_3)_2(CHOCH_3)^+CF_3SO_3^-$. *mer,trans*-$Re(CO)_3(PPh_3)_2(CHOCH_3)^+CF_3SO_3^-$ (0.20 g, 0.20 mmol) was stirred in 6 mL of CH_2Cl_2 at 0 °C in a Schlenk flask. A slurry of $NaBH_4$ (0.015 g, 0.40 mmol) in 10 mL of methanol was added. The yellow solution immediately became colorless, and a white precipitate began to form. After the evolution of gas had ceased (~10 min), the reaction mixture was filtered to collect the product. This was recrystallized in CH_2Cl_2 (4 mL) and pentane (6 mL) to give white crystals of **4** (0.15 g, 90% yield); mp 169 °C dec. Anal. Calcd for $C_{41}H_{35}O_4P_2Re$: C, 58.63; H, 4.20. Found: C, 58.37; H, 4.21. IR (CH_2Cl_2): ν_{CO} 2030 (vw), 1920 (s), 1880 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.51 (m), 3.23 (t, J_{PH} = 6.8 Hz), 2.50 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 197.7 (t, J_{PC} = 9.6 Hz), 196.4 (t, J_{PC} = 6.3 Hz), 136.0 (t, J_{PC} = 23.3 Hz), 133.7 (t, J_{PC} = 5.5 Hz), 129.9 (s), 128.3 (t, J_{PC} = 4.8 Hz), 64.8 (s), 62.0 (t, J_{PC} = 7.1 Hz).

Method 2. From *mer,trans*-$Re(CO)_3(PPh_3)_2CHO$. To a stirred solution of $CF_3SO_3CH_3$ (0.027 mL, 0.24 mmol) in 12 mL of CH_2Cl_2 maintained at 0 °C was added *mer,trans*-$Re(CO)_3(PPh_3)_2CHO$ (0.20 g, 0.24 mmol) in several additions over the course of 2 min. After an additional 5 min, a slurry of $NaBH_4$ (0.18 g, 0.48 mmol) in 10 mL of CH_3OH was added. The yellow reaction solution immediately became colorless, and a white precipitate began to form. After the evolution of gas had ceased (~10 min), the reaction mixture was filtered and the product rinsed with 15 mL of CH_3OH. The product was dried in vacuo to give 0.18 g (89% yield).

Preparation of *mer,trans*-$Re(CO)_3[P(OPh)_3]_2(CH_2OCH_3)$ (5). The following procedure was performed in a nitrogen-filled glovebox. $CF_3SO_3CH_3$ (19.5 μL, 0.172 mmol) was dissolved in 5 mL of CH_2Cl_2 (distilled from P_2O_5), and the mixture was chilled to −20 °C. *mer,trans*-$Re(CO)_3[P(OPh)_3]_2CHO$ (0.311 g, 0.338 mmol) was added, and the mixture was stirred at −20 °C for 30 min. The solution was concentrated under vacuum, to 2 mL, hexane (10 mL) was added, and the mixture was stirred at −20 °C for an additional 30 min. The mixture was filtered through Celite, and the precipitate was saved. Solvent was removed from the filtrate under vacuum at ambient temperature, the residue was dissolved in 1 mL of CH_2Cl_2, and hexane (10 mL) was added. The flask was stoppered, sealed with Parafilm, and then removed from the glovebox and chilled to −30 °C. All further manipulations were performed outside the glovebox. White crystals formed over a 3-day period, were collected by filtration, and dried, in vacuo (0.097 g, 61% yield); mp 124–126 °C dec. Anal. Calcd for $C_{41}H_{35}O_{10}P_2Re$: C, 52.62; H, 3.77. Found: C, 52.34; H, 3.77. IR (CH_2Cl_2): ν_{CO} 2060 (w), 1965 (s), 1930 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.24 (m), 3.93 (t, J_{PH} = 7.9 Hz), 3.15 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 191.9 (t, J_{PC} = 14.0 Hz), 189.0 (t, J_{PC}= 8.7 Hz), 151.8 (t, J_{PC} = 3.6 Hz), 130.0 (s), 125.2 (s), 121.6 (s), 65.2 (s), 54.6 (t, J_{PC} = 10.7 Hz). The precipitate saved from above was dissolved in CH_2Cl_2, the solution was filtered through Celite and then concentrated to 2 mL. Anhydrous ether (20 mL) was added, and the solution was chilled to −30 °C for 3 days to give *trans*-$Re(CO)_4[P(OPh)_3]_2^+CF_3SO_3^-$ as white crystals (0.115 g, 64% yield). The spectral properties were identical with those reported for the BF_4 salt.[12]

Preparation of $CpMo(CO)_2[P(OPh)_3](CH_2OCH_3)$ (6). A 0.126-g sample (0.660 mmol) of *p*-toluenesulfonic acid monohydrate was dissolved in 15 mL of methanol/CH_2Cl_2 (1.5:8.5) and then chilled to −40 °C. $CpMo(CO)_2[P(OPh)_3]CHO$ (0.370 g, 0.660 mmol) was then added in portions during 1 min. Solvent was then removed under vacuum, and the residue was extracted with

4×10 mL of hexane. The combined extracts were filtered through Celite; the insoluble residue was saved. Concentrating the filtrate to about 10 mL and chilling to 0 °C for several hours yielded 0.157 g of a yellow-orange solid. The ^{1}H NMR of the solid ($CDCl_3$) indicated the presence of **6**, $CpMo(CO)_2[P(OPh)_3]CH_3$,[16] and the metallacycle $CpMo(CO)_2[P(OPh)_2(o\text{-}OC_6H_4CH_2)]$[19] at about a 32:9:1 (Cp) integral ratio, respectively. The mixture was separated on a Florosil column, eluting with hexane, 1:10 CH_2Cl_2/hexane, and finally CH_2Cl_2. The latter fractions were evaporated to dryness, and the residue was dissolved in 10 mL of hexane. Chilling to −30 °C gave 0.120 g (63%) of yellow **6**. IR (hexane): ν_{CO} 1967 (m), 1890 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): trans δ 7.30 (m), 4.66 (d, $J_{PH} = 1.1$ Hz), 4.58 (d, $J_{PH} = 3.8$ Hz), 3.30 (s); cis δ 7.30 (m), 4.85 (s), CH_2 signal not distinct, 3.35 (s). The cis:trans ratio is 1:9, respectively [lit.[16] ^{1}H NMR ($CDCl_3$): trans δ 4.62 (d, $J_{PH} = 1.2$ Hz), 4.60 (d, $J_{PH} = 3.6$ Hz), 3.31 (s); cis δ 4.78 (s), 3.56 (s), CH_2 signal not distinct]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): trans δ 232.6 (d, $J_{PC} = 34.6$ Hz), 151.2 (d, $J_{PC} = 7.3$ Hz), 129.6 (s), 125.0 (s), 121.8 (d, $J_{PC} = 4.4$ Hz), 91.7 (s), 64.0 (d, $J_{PC} = 13.2$ Hz), 63.4 (s); cis δ 124.8 (s), 121.6 (d, $J_{PC} = 4.7$ Hz), 91.5 (s), 63.6 (d, $J_{PC} = 31.4$ Hz), other signals for this isomer not visible. After determination of the yield of **6**, the yields of the methyl complex and the metallacycle were calculated on the basis of the ^{1}H NMR ratio as 27% and 2%, respectively. The hexane-insoluble residue from above was dissolved in CH_2Cl_2, extracted with 2×20 mL of water, and then dried over $MgSO_4$. After filtration, the filtrate was evaporated to dryness and dried under vacuum to give a yellowish red oily material (0.158 g, 61%), whose IR and NMR spectra were consistent with its formulation as $CpMo(CO)_3[P(OPh)_3]^+OTs^-$. IR ($CH_2Cl_2$): ν_{CO} 2071 (s), 2010 (m, sh), 1984 (vs, br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.38 (m), 5.61 (s), 2.29 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 222.4 (d, $J_{PC} = 40.8$ Hz), 221.0 (d, $J_{PC} = 3.1$ Hz), 94.4 (s), 21.22 (s). The phenyl carbons are omitted. The spectral properties were similar to those of $CpMo(CO)_3[P(OPh)_3]^+BF_4^-$.[12]

Reaction of *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHOH)^+$-$CH_3C_6H_4SO_3^-$ with CH_3OH. To 20 mL of a 1:1 mixture of CH_2Cl_2 and CH_3OH at room temperature was added *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHOH)^+CH_3C_6H_4SO_3^-$ (0.20 g, 0.23 mmol) with stirring. The yellow solution was stirred for 3 h, at which time the solvent was removed under vacuum. The yellow residue was recrystallized from CH_2Cl_2/pentane to give yellow crystals of *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHOCH_3)^+CH_3C_6H_4SO_3^-$ contaminated with a small amount of *trans*-$Mn(CO)_4(PPh_3)_2^+$-$CH_3C_6H_4SO_3^-$; the yield was 0.10 g (50%). IR (CH_2Cl_2): ν_{CO} 2050 (w), 1965 (s, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 11.8 (s), 7.4 (m), 3.5 (s), 2.4 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 338.2 (br s), 220.0 (t), 216.8 (t), 77.5 (s), 21.4 (s). The phenyl peaks are omitted. The spectral properties are comparable to those reported for *mer,trans*-Mn-$(CO)_3(PPh_3)_2(CHOCH_3)^+CF_3SO_3^-$.[13b]

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[19] The structure of this compound has been confirmed by X-ray crystallography; the details of its characterization will be reported elsewhere (D. H. Gibson, J. O. Franco, and J. F. Richardson, unpublished results).

Synthesis, NMR Spectra, and Molecular Orbital Calculations of Ruthenium and Osmium Dications of the Type $[C_5Me_5MC_5Me_3(CH_2)_2]^{2+}$

A. Z. Kreindlin, E. I. Fedin, P. V. Petrovskii, and M. I. Rybinskaya*
Nesmeyanov Institute of Organoelement Chemistry, USSR Academy of Sciences, Moscow, USSR

R. M. Minyaev and R. Hoffmann*
Department of Chemistry, Cornell University, Ithaca, New York 14853

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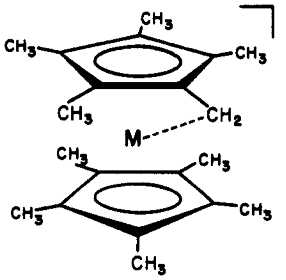
Summary: Starting from decamethylated metallocenes, $(Me_5C_5)_2M$ (M = Ru, Os), we generated a mixture of aldehydes, from which the dialdehydes were separated and reduced to dicarbinols. These were used to obtain a mixture of dications, consisting primarily of the 1,2-isomers $[C_5Me_5MC_5Me_3(CH_2)_3]^{2+}$ (M = Ru, Os), as well as their 1,1′-isomers, $[(C_5Me_4CH_2)M(C_5Me_4CH_2)]^{2+}$ (M = Ru, Os). ^{1}H and ^{13}C NMR spectra support the assigned structures. Molecular orbital calculations on the predominant 1,2-dication indicate substantial bending of the CH_2^+ groups out of the plane of the Cp ring, canting of the ring, and off-center slipping, deformations comparable to those occurring in the parent dication.

We have previously synthesized and studied stable Ru- and Os-containing monocations of the type $[C_5Me_5MC_5Me_4CH_2]^+$ (M = Ru, Os).[1,2] It was thus established experimentally that the donor–acceptor interaction between a primary α-carbocation center and an unshared electron pair on the metal in a metallocene may be sufficiently strong to form a true M–C σ bond (2.24 Å, M = Os; 2.27 Å, M = Ru; typical literature values for such σ bonds are ~2.22 Å).[3]



In these cations the CH_2 group is strongly bent toward the metal, moving out of the plane of the cyclopentadienyl ring by 41.8° (M = Os) and 40.3° (M = Ru) and essentially losing its carbocation character. At the same time the metallocene structure of these cations is relatively little distorted (some detailed geometrical parameters will be presented below).

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