Tetrahedral mixed-metal clusters containing bridging sulfido ligands. Synthesis and crystal and molecular structures of PtOs3(CO)8(PMe2Ph)3(.mu.3-S) and Os3W(CO)11(PMe2Ph)2(.mu.3-S)

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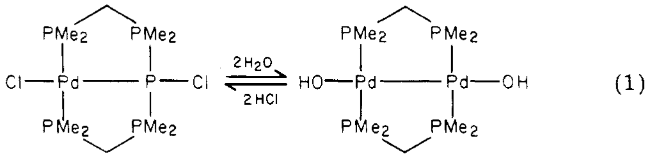
Organometallics, **1984**, 3 (4), 634-636• DOI: 10.1021/om00082a024 • Publication Date (Web): 01 May 2002 in D_2O compared to CD_2Cl_2 or CD_3CN reveal little about the differences in identity of 1 in aqueous vs. nonaqueous solvents.[27] However, significant differences in the electronic absorption spectra in aqueous solutions are observed. In H_2O, the UV-vis spectra of 1 exhibits the same features as those seen in CH_2Cl_2 or CH_3CN, but uniformly red-shifted by ~15 nm. The identity of 1 in aqueous solution is largely established by the following set of observations. The addition of $AgBF_4$ to aqueous solutions of 1 leads to precipitation of AgCl and no apparent change in the UV-vis spectrum. This result contrasts strongly to that obtained in CH_3CN solution where spectra obtained before and after AgCl precipitation are markedly different. The addition of Cl^- to aqueous solutions of 1 leads to a blue shift of the spectrum such that in 1 M NaCl the observed UV-vis spectrum is remarkably similar to those obtained in CH_2Cl_2 or CH_3CN solutions without excess chloride. The UV-vis spectra of 1 in H_2O and 1 M aqueous NaCl are presented in Figure 2. Conductivity data suggest that at pH 7, 1 is a neutral complex in H_2O. When 1 is dissolved in aqueous solution, the pH decreases and the solution conductivity increases to a value consistent with a 1:1 electrolyte.[27] These results suggest that liberation of 2 equiv of HCl accompanies dissolution of 1 in H_2O. We note that addition of excess NaCl to aqueous solutions of 1 results in an increase in pH consistent with the reversibility of eq 1. Raman spectra for 1 in H_2O display

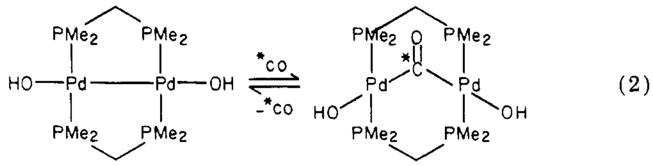


(1)

1 3

ν(Pd-Pd) = 140 cm^{-1}, consistent with related Pd-Pd bonded diphosphine-bridged complexes.[40] Raman spectra in H_2O also reveal no bands assignable to ν(Pd-Cl).[40] However, a band at 351 cm^{-1} in H_2O is consistent with ν(Pd-O). These observations collectively point to the identity of 1 in aqueous solution as a neutral, Pd-Pd-bonded binuclear complex, resulting from the substitution of hydroxide for chloride in the positions trans to the Pd-Pd bond, eq 1, to give $Pd_2(OH)_2(dmpm)_2$ (**3**). In an apparently similar reaction, treatment of 1 with 2 equiv of NaOPh leads to $Pd_2(OPh)_2(dmpm)_2$ (**4**).

The hydroxide (3) and phenoxide (4) are reactive with respect to the insertion of CO into Pd-Pd and Pd-OR (R = H, Ph) bonds. The treatment of 3 with ^{13}CO in neutral aqueous solution leads initially to Pd-Pd bond insertion, eq 2, to give $Pd_2(OH)_2(\mu\text{-}^{13}CO)(dmpm)_2$.[41] The similarities in ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR data of 2[28] and 5[41] suggest that the aqueous solution structure of 5 is similar to the structurally characterized 2. Significantly, the $^{31}P\{^1H\}$ NMR signal for ^{13}CO-enriched 5 is a first-order doublet (J_{P-C} = 5.4 Hz), consistent with a single bridging CO.



(2)

3 5

Preliminary investigations with the diphenoxide complex (4)[42] suggest that CO insertion into Pd-OPh bonds occurs concurrently with Pd-Pd bond insertion. Spectroscopic data[43] are consistent with the formulation of the product as a diphenyl ester of a dipalladium carboxylic acid, $Pd_2(COPh)_2(\mu\text{-}CO)(dmpm)_2$. Heating the ^{13}CO-enriched diester leads to quantitative evolution of $^{13}CO_2$ and formation of $Pd_2(Ph)_2(\mu\text{-}^{13}CO)(dmpm)_2$.[44] The insertion of CO into the Pd-OR (R = H, Ph) bonds of the new complexes reported herein is the subject of our ongoing investigation. Studies of the insertion of other substrates, notably olefins and acetylenes, into Pd-Pd and Pd-OR are in progress.

Acknowledgment. This research was supported in part by the DOE through a grant administered through the Energy Policy Research and Information Program at Purdue University. We also thank Conoco, Inc., and Nalco Chemical Co. for grants administered through the Coal Research Center at Purdue University for their support of this research. The assistance of Prof. W. R. Robinson, Prof. S. Byrne, and E. Martinez in the collection of X-ray data and the crystal-structure solution; and of D. Whittern in obtaining NMR spectra is gratefully acknowledged. The DEC 11/60 computer and X-ray Structure Solution Package in the Department of Chemistry were purchased with funds from NSF Grant CHE-8204994. This support is gratefully acknowledged. The Raman spectra of Pd-Pd binuclear complexes have been carried out in collaboration with Prof. Richard F. Dallinger, whose cooperation is greatly appreciated.

Supplementary Material Available: Positional parameters, temperature factors, bonding and selected nonbonding distances, bond angles, and observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

Tetrahedral Mixed-Metal Clusters Containing Bridging Sulfido Ligands. Synthesis and Crystal and Molecular Structures of $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$ and $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)$

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Summary: The new tetrahedral mixed-metal cluster compounds $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$ (**2**) and $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)$ (**4**) have been prepared by the reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ (**1**) with $Pt(PMe_2Ph)_4$ upon mixing at room temperature and with $W(CO)_5(PMe_2Ph)$ in the presence of UV irradiation in yields of 26% and 27%, respectively, and have been characterized by single-crystal X-ray diffraction methods.

Mixed-metal cluster compounds represent an important and rapidly developing new area of transition-metal cluster chemistry.[1] These compounds can serve as intermediates in the synthesis of novel heterogeneous catalysts[2] or as precursors to homogeneous catalysts.[3] Chiral tetranuclear

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(1) (a) Roberts, D. A.; Geoffroy, G. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford 1982; Chapter 40. (b) Bruce, M. I. *J. Organometal. Chem.* **1983**, *257*, 417.

(2) Ichikawa, M. *J. Catal.* **1979**, *56*, 127.

(3) (a) Muetterties, E. L.; Krause, M. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 135. (b) Whyman, R. In "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980; Chapter 8.

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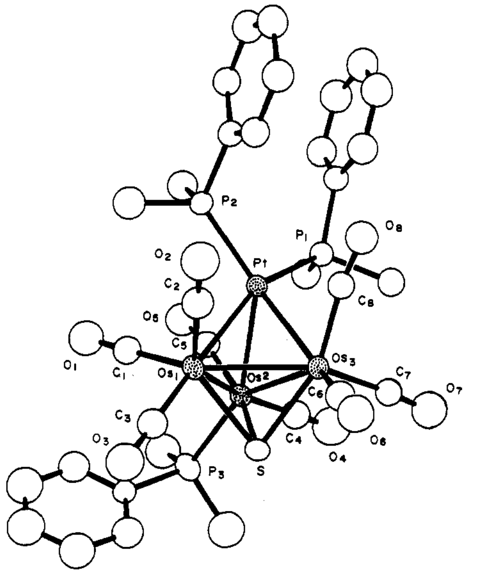

Figure 1. ORTEP diagram of $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$ (**2**) showing 50% probability thermal ellipsoids.

clusters could yield catalysts that produce asymmetric induction.[3b,4] It has been shown that bridging ligands can be of great value in the synthesis and stabilization of cluster compounds.[1] We have now found that the sulfido-bridged cluster $Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$[5] is a useful reagent for the synthesis of tetrahedral mixed-metal cluster compounds of elements of the third transition series.

$Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ (**1**) (0.041 mmol) and $Pt(PMe_2Ph)_4$ (0.054 mmol) were allowed to react for 1 h at room temperature in 50 mL of THF solvent. Three compounds were isolated by TLC. The first (red in color), obtained in 26% yield, was shown by a single-crystal X-ray diffraction analysis to have the formula $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$ (**2**).[6] The molecular structure of **2** is shown in Figure 1.[7,8] The molecule consists of a cluster of one platinum and three osmium atoms arranged in the shape of a distorted tetrahedron.[9] The platinum atom is unsymmetrically bonded to the triosmium group such that one osmium–platinum distance, Os(1)–Pt = 2.853 (1) Å, is considerably longer than the other two, Os(2)–Pt = 2.740 (1) Å and Os(3)–Pt = 2.766 (1) Å. These distances are similar to those observed in the electron-deficient cluster $H_2PtOs_3(CO)_{10}[P(C_6H_{11})_3]$ prepared by the reaction of $H_2Os_3(CO)_{10}$ with $Pt(C_2H_4)_2P(C_6H_{11})_3$.[10] The osmium–osmium bonding is also quite irregular, with two osmium–osmium bonds, Os(1)–Os(2) = 2.816 (1) Å and Os(1)–Os(3) = 2.770 (1) Å, being significantly shorter than the third, Os(2)–Os(3) = 3.064 (1) Å. $Os_4(CO)_{12}(\mu_3\text{-}S)$ (**3**) is the homonuclear analogue of **2**.[11] In **3** the sulfur-bridged osmium–osmium distances are essentially equal and average 2.864 (3) Å. The reason for the excessive lengthening of the Os(2)–Os(3) bond in **2** is not clear, but this could be influenced by the phosphine ligands.[12] A triply bridging sulfido ligand is bonded to the triosmium group. The Os–S distances range from 2.315 (2) to 2.406 (2) Å. Compound **2** contains three PMe_2Ph ligands. Two are bonded to the platinum atom and one is bonded to Os(2). The latter was probably added via ligand substitution reaction involving "free" phosphine, presumably released from the $Pt(PMe_2Ph)_4$ reagent. There are eight carbonyl ligands. All are of a linear terminal type, except C(8)–O(8), which is semibridging from Os(3) to Pt. The facile synthesis of **2** contrasts with the reaction of $Os_3(CO)_{12}$ with $Pt(PMePh_2)_4$ which yields only the phosphine derivatives $Os_3(CO)_{12-x}[(PMePh_2)_3]_x$, x = 1, 2, after 3 days.[13]

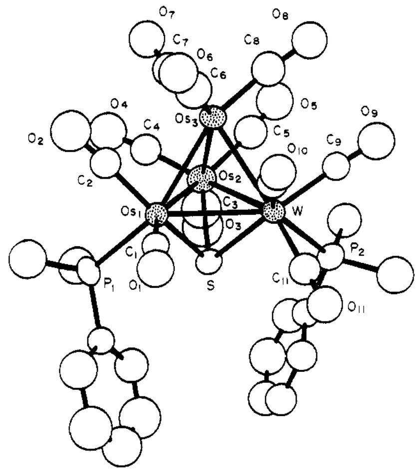

Figure 2. ORTEP diagram of $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)$ (**4**) showing 50% probability thermal ellipsoids.

When hexane solutions of **1** (0.030 mmol) and $W(CO)_5(PMe_2Ph)$ (0.090 mmol) are irradiated (UV) for 1 h under a slow purge with N_2, the compound $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)$ (**4**) is formed and isolated (TLC) as the major product in 27% yield.[14] The formula and structure of **4** were established by single-crystal X-ray diffraction methods.[7,15] An ORTEP drawing of the molecule is shown in Figure 2.[16] The cluster consists of one tungsten and

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[4] (a) Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 864. (b) Richter, F.; Vahrenkamp, H. *Ibid.* **1980**, *19*, 65. (c) Muller, M.; Vahrenkamp, H. *Chem. Ber.* **1983**, *116*, 2748.

[5] Adams, R. D.; Horváth, I. T.; Kim, H. S. *Organometallics*, in press.

[6] For **2**, IR (in hexane) 2040 (s), 1998 (s), 1969 (s), 1945 (m, br), 1919 (m), and 1891 (w) cm^{-1}; ^{1}H NMR (in $CDCl_3$) at room temperature δ 7.19–7.66 (m, 15 H), 2.34 (d, 6 H, J^2_{P-H} = 10.3 Hz), 1.73 (q, 12 H, J^2_{P-H} = 10.0 Hz, $J_{Pt-H} \approx 25$ Hz). **2** is stereochemically nonrigid, but at reduced temperatures the expected inequivalences of the diastereotopic methyl resonances of the phosphine ligands can be observed. The second compound isolated from this reaction is orange-brown and has been identified as $PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$, 25% yield; IR (hexane) 2090 (s), 2020 (vs), 2015 (s, sh), 2010 (s), 1983 (vw), 1959 (m), 1921 (m), and 1915 (m, sh) cm^{-1}. The third product (12 mg) has not yet been identified, but its IR spectrum shows absorptions at 2053 (vs), 2003 (s), 1992 (2), 1976 (vs), 1961 (m), 1928 (m), 1908 (m), 1895 (w, sh) cm^{-1}.

[7] Intensity data were collected on an Enraf-Nonius CAD-4 automatic diffractometer by using Mo K$\bar{\alpha}$ radiation and the ω-scan technique. All calculations were performed on a Digital Equipment corp. PDP 11/45 computer by using the Enraf-Nonius SDP program library, version 18.

[8] Space group: $P\bar{1}$; a = 9.761 (4) Å, b = 11.926 (5) Å, c = 16.412 (6) Å, α = 78.57 (3)°, β = 89.16 (3)°, γ = 87.98 (4)°, V = 1871 (2) Å^3. Z = 2, ρ_{calcd} = 2.50 g/cm^3. The structure was solved by the heavy-atom method. After correction for absorption, full-matrix least-squares refinement (4223 reflections, $F_o^2 \geq 3.0\sigma(F^2)$) yielded the residuals R = 0.032, R_w = 0.037.

[9] Selected interatomic distances (Å) and angles (deg) for **2** are as follows: Os(1)–Os(2) = 2.816 (1), Os(1)–Os(3) = 2.770 (1), Os(2)–Os(3) = 3.064 (1), Os(1)–Pt = 2.853 (1), Os(2)–Pt = 2.740 (1), Os(3)–Pt = 2.766 (1), Os(1)–S = 2.406 (2), Os(2)–S = 2.315 (2), Os(3)–S = 2.350 (2); Pt–Os(3)–C(8) = 66.33 (26), Os(3)–C(8)–O(8) = 168.7 (8).

[10] Bruce, M. I.; Shaw, G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1781.

[11] Adams, R. D.; Foust, D. F.; Mathur, P. *Organometallics* **1983**, *2*, 990.

[12] Adams, R. D.; Horváth, I. T.; Segmüller, B. E.; Yang, L. W. *Organometallics* **1983**, *2*, 144.

[13] Farrugia, L.; Howard, J. A. K.; Mitrprachachon, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1981**, 155.

[14] For **4**, IR (in hexane): 2070 (m), 2063 (sh), 2030 (w), 2009 (sh), 1996 (s), 1983 (sh), 1966 (w), 1946 (w), 1933 (w), 1911 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.47 (m, 5 H), 2.23 (d, 3 H, J^2_{P-H} = 9.1 Hz), 2.08 (d, 3 H, J^2_{P-H} = 10.2 Hz).

[15] Space group: $P2_1/n$; a = 14.631 (6) Å, b = 12.654 (3) Å, c = 19.354 (6) Å, β = 106.32 (3)°, V = 3439 (4) Å^3, Z = 4, ρ_{calcd} = 2.65 g/cm^3. The structure was solved by direct methods (MULTAN, 284 reflections, $E \geq 2.11$). After correction for absorption, full-matrix least-squares refinement (3251 reflections, $F_o^2 \geq 3.0\sigma(F^2)$) yielded the residuals R = 0.055 and R_w = 0.068.

three osmium atoms arranged in the shape of a distorted tetrahedron. A sulfido ligand bridges one of the tungsten–diosmium faces. The osmium–osmium distances range from 2.798 (1) to 2.870 (1) Å while the tungsten–osmium distances are similar and range from 2.827 (1) to 2.947 (1) Å. The molecule contains two PMe_2Ph ligands; one is bonded to the tungsten atom, the other to osmium Os(1). As in **2** the osmium-coordinated phosphine ligand must have originated with the $W(CO)_5(PMe_2Ph)$ reagent which was used in excess. Compound **4** contains 11 carbonyl ligands. C(10)–O(10) could be weakly semibridging from W to Os(3).

It has been shown that triply bridging sulfido ligands can be valuable for the synthesis of cluster compounds by virtue of their ability to coordinate to electron-deficient metal-containing moieties by using their lone pair of electrons.[17] Such a process can be inferred in the formation of **4** since the tungsten atom is bonded to the sulfido ligand. However, in **2** there is no interaction between the platinum atom and the sulfido ligand although this does not prove that none had occurred at some stage in its formation. It is possible that the platinum moiety in **2** may have been added to **1** via direct formation of platinum–osmium bonds. Further investigations of the minor products in these reactions should provide evidence for the mechanisms of formation. At present, it is clear that sulfido-bridged clusters such as **1** can be useful in the synthesis of tetrahedral mixed-metal clusters of the third transition series.

Acknowledgment. This research was supported by the National Science Foundation, Grant No. CHE-8019041. NMR studies were supported by Grant No. CHE-7916210 to the Northeast Regional NSF-NMR Facility from the National Science Foundation. We wish to thank Engelhard Industries for a loan of osmium tetraoxide.

Supplementary Material Available: Tables of structure factor amplitudes, fractional atomic coordinates, bond distances, and bond angles for both structures (39 pages). Ordering information is given on any current masthead page.

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(16) Selected interatomic distances (Å) and angles (deg) for 4 are as follows: Os(1)–Os(2) = 2.831 (1), Os(1)–Os(3) = 2.798 (1), Os(2)–Os(3) = 2.870 (1), Os(1)–W = 2.947 (1), Os(2)–W = 2.913 (1), Os(3)–W = 2.827 (1), Os(1)–S = 2.311 (4), Os(2)–S = 2.396 (4), W–S = 2.37 (4), Os(3)–W–C(10) = 64.6 (5), W–C(10)–O(10) = 168.3 (14).

(17) (a) Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 444. (b) Seyferth, D.; Henderson, R. S.; Fackler, J. P., Jr.; Mazany, A. M. *J. Organomet. Chem.* **1981**, *213*, C21. (c) Adams, R. D.; Männig, D.; Segmüller, B. E. *Organometallics* **1983**, *2*, 149.

Sequential Insertion of Carbon Monoxide and Olefins into Alkylmanganese Complexes. Applications of High-Pressure Techniques

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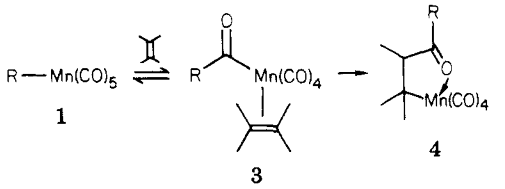
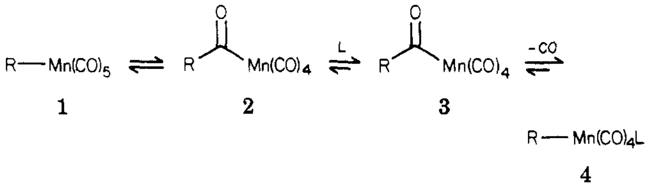
Summary: Methyl- and benzylmanganese pentacarbonyl underwent sequential migratory insertion of carbon monoxide followed by reaction with norbornylene and cyclopentene to produce manganese complexes **5**–**7**. In several instances, high-pressure conditions (3–4 kbar) were required to obtain good yields of adducts. Complexes **5**–**7** are shown to be valuable intermediates in organic synthesis.

Scheme I



The insertion of carbon monoxide into transition-metal–alkyl bonds is a key feature in a variety of processes involving heterogeneous and homogeneous transition-metal catalysts (Fischer–Tropsch chemistry, hydroformylation, the Oxo process, etc.). There are numerous reports of organometallic complexes which will insert carbon monoxide into the metal–alkyl bond to produce metal–acyl complexes.[1] One of the most widely investigated systems of this type is the alkylmanganese pentacarbonyl system which was initially studied by Calderazzo[2] and later by others, most notably Casey and Flood.[3] For methylmanganese pentacarbonyl (**1**, R = Me) it has been demonstrated that the methyl group migrates to an adjacent carbon monoxide ligand, presumably to generate a coordinatively unsaturated manganese complex, **2**, which then adds an additional ligand (either CO or PPh_3) to produce the observed acyl complex **3**.[2,3] Not all migratory insertions occur as readily as methyl, however. For instance, benzylmanganese pentacarbonyl (**1**, R = $PhCH_2$) does not undergo migratory insertion in the presence of ligands such as carbon monoxide, phosphines, or phosphites.[4] The acyl complex **3** (R = $PhCH_2$) is thermodynamically unstable with regard to **1** and undergoes decarbonylation,[5,6]



An associative process, of which the migratory insertion reaction **1** → **3** is a prime example, should be facilitated by increasing the reaction pressure.[7] Since the enthalpy

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(1) For leading references see: Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books; Mill Valley, CA; 1980; pp 260–288. Kuhlman, E. J.; Alexander, J. *Coord. Chem. Rev.* **1980**, *33*, 195–225. Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 88.

(2) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101 and references cited therein. Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.

(3) Casey, C. P.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 1166 and references cites therein. Flood, T. C., Jensen, J. E.; Statler, J. A. *Ibid.* **1981**, *103*, 4410. Flood, T. C. *Top. Stereochem.* **1980**, *12*, 37.

(4) Calderazzo, F.; Cotton, F. A. "Abstracts of Papers", 7th International Conference on Coordination Chemistry, June 1962, Stockholm, Paper 6117.

(5) Drew, D.; Darensbourg, M. Y.; Darensbourg D. J. *J. Organomet. Chem.* **1975**, *85*, 73.

(6) Alexander has shown that isocyanates promote migratory insertion of carbon monoxide in the benzyl manganese complex. Alexander, J. J.; Katy, D. W. *Inorg. Chem.* **1978**, *17*, 1489.

(7) This stratagem has been successfully applied to many organic reactions[8] and to at least one organometallic system.[9]

(8) Dicken, C. M.; DeShong, P. *J. Org. Chem.* **1982**, *47*, 2047 and references cited therein. Isaacs, N. S. "Ligand Phase High Pressure Chemistry"; Wiley-Interscience: New York, 1981.

(9) The oxidative addition of methyl iodide to trans $[Ir(CO)Cl(PPh_3)_2]$ has been shown to have activation volumes ranging from -15.2 cm^3 mol^{-1} to -29.8 cm^3 mol^{-1} depending upon the solvent employed. Steiger, H.; Kelm, H. *J. Phys. Chem.* **1973**, *77*, 290.

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