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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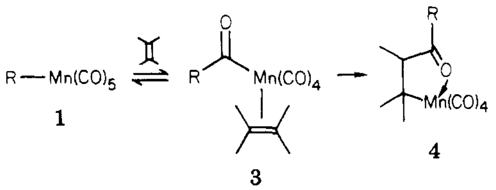
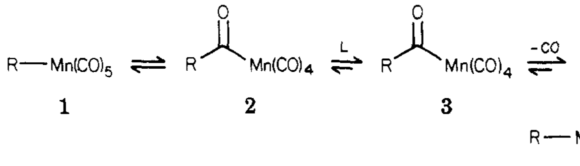
Summary: Methyl- and benzylmanganese pentacarbonyl underwent sequential migratory insertion of carbon monoxide followed by reaction with norbornylene and cyclopentene to produce manganese complexes **5-7**. In several instances, high-pressure conditions (3-4 kbar) were required to obtain good yields 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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Table I. Reactions of 1 with Alkenes[a]

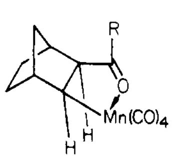
manganese complex	alkene	pressure, kbar[b]	temp, °C[b]	product[c]	yield, %[d]
1, R = CH$_3$	norbornylene	1	25	5	81
		3.9	25		91
1, R = CH$_2$Ph	norbornylene	1	25	6[e]	0
		1	50		6
		3.9	25		84
1, R = CH$_3$	cyclopentene	1	25	7[e]	0
		1	50		0
		2.9	30		29

[a] In a typical experiment complex 1 was dissolved in THF containing an excess of olefin (~2 equiv), and the solution was placed in a Teflon tube *b* and pressurized. [b] See ref 14 for a description of the apparatus and reaction vessel. [c] All products gave satisfactory IR, ^{1}H NMR, ^{13}C NMR, and MS data. The data for each compound are compiled in the supplementary material. [d] Yield of isolated product. All products were purified by chromatography on silica prior to spectroscopic analysis. [e] A single diastereomer was produced.

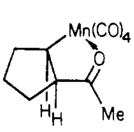
of a reaction at equilibrium is not significantly altered by increasing the reaction pressure,[10] the change in free energy for the reaction is a result of change in the entropy of the system. *If the volume change for the associative process is −20 cm^3 mol^{-1}, then the associative reaction is ~42 kcal mol^{-1} more exothermic when performed at solution pressures of 5 kbar. Therefore, it should be possible to prepare and stabilize metal–acyl complexes using high-pressure techniques and to investigate subsequent reactions of these complexes.*

In this Communication, we present results that demonstrate that alkylmanganese pentacarbonyl complexes (1) undergo sequential migratory insertion at solution pressures of 3–4 kbar and that the resulting acyl complexes 3 react with norbornylene and cyclopentene to yield products derived from addition of the acyl–manganese bond across the unsaturated linkage (4; see Scheme I).[11,12] In the absence of pressure, the insertion reactions proceed sluggishly and in low yield, if at all.

The results obtained from the reaction of methyl- and benzylmanganese pentacarbonyl with norbornylene and cyclopentene are presented in Table I and indicate that methylmanganese pentacarbonyl (1, R = Me) reacts with norbornylene at atmospheric pressure, as well as at 3.9 kbar, to produce adduct 5, which arises from migratory insertion of carbon monoxide followed by addition of the resulting acylmanganese complex (3) across the olefinic linkage. The reaction of 1 and norbornylene gave 5 without resorting to high-pressure conditions. However, complex 1 and the unreactive olefin cyclopentene gave no adduct 7 at atmospheric pressure even after long reaction times and/or heating. On the other hand, when the reaction mixture of 1 and cyclopentene was pressurized to 2.9 kbar, adduct 7 was produced in 29% yield. The adduct 7 was only obtained under high-pressure conditions.



5, R = Me
6, R = CH$_2$Ph



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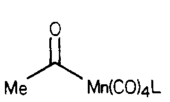

8, L = CO
9, L = PPh$_3$

A single diastereomer of 5 and 7 was produced in the reactions, but the relative stereochemistry of the adducts could not be deduced from the spectroscopic data. The stereochemistry of 5 was proven by subsequent reaction with LiBEt$_3$H (vide infra).[13]

Unlike methylmanganese pentacarbonyl, the benzyl complex (1; R = CH$_2$Ph) did not yield adducts in the reaction with norbornylene at room temperature and gave only a 6% yield of adduct 6 at 50 °C. However, at solution presssures of 3.9 kbar/25 °C an 84% yield of 6 was obtained. Again a single diastereomer of 6 was formed, and the stereochemistry has been assigned on the basis of the studies with 5, the methyl analogue. It is noteworthy that in this instance as in the reaction of 1 with cyclopentene only high-pressure techniques were successful in producing acyl insertion products. In those cases in which the migratory insertion product (3) is disfavored in the equilibrium between 1 and 3 (i.e., R = CH$_2$Ph[4,6]), high-pressure techniques lead to improved yields of adducts.

The addition of the acylmanganese complex across the olefinic linkage requires that the olefin function as a ligand on manganese (as in 3). The coordinatively saturated manganese complexes 8 and 9 did not react with norbornylene, even at pressures of 4.0 kbar.

The complexes resulting from addition of the acyl–manganese bond across the olefinic bond (5–7) are remarkably stable[15] and display no tendency toward multiple olefin insertion, multiple carbon monoxide insertion, or β-hydride elimination. Also, the oxygen of the acyl group is not readily displaced by other ligands. For instance, treatment of 5 with trimethyl phosphite resulted in the formation of 10, rather than displacement of the acyl function. The exceptional stability of the five-membered system in 5–7 presumably functions as a "thermodynamic trap" in the reaction.

Adducts 5–7 have proven to be valuable intermediates in organic synthesis. For instance, treatment of 5 with LiBEt$_3$H at −78 °C resulted in formation of lactone 11 in

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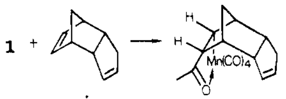
(10) Hepler, L. G. *J. Phys. Chem.* **1965**, *69*, 965. Twigg, N. V. *Inorg. Chim. Acta* **1977**, *24*, 184.

(11) Wimp and his co-workers have shown that acylmanganese complexes will add to double bonds which are held intramolecularly in the complex. Roberton, J. B.; Wimp, P. O. *Inorg. Chem.* **1973**, *12*, 1740 and references cited therein.

(12) These complexes are chemically and spectroscopically similar to complexes reported by Haszeldine. Booth, B. L.; Gardner, M.; Haszeldine, R. N. *J. Chem. Soc., Dalton Trans.* **1975**, 1856.

(13) This result is in contrast with the report of Haszeldine[12] which concludes from spectroscopic evidence that 1 (R = Me) and i react to produce the endo isomer ii.

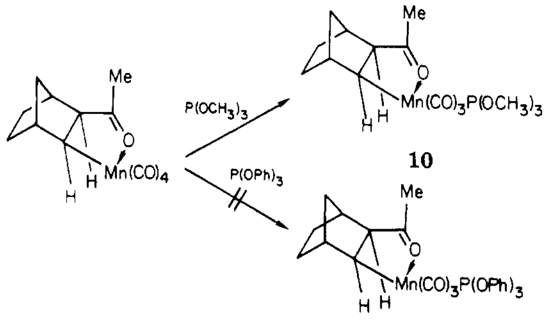


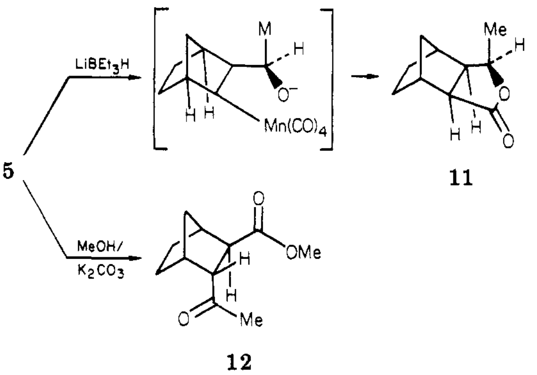
i

ii

(14) DeShong, P.; Dicken, C. M.; Perez, J. J.; Shoff, R. M. *Org. Prep. Proced. Int.* **1983**, *14*, 369.

(15) Omae has commented upon the exceptional stability associated with five-membered coordination systems. Omae, I. *Coord. Chem. Rev.* **1980**, *32*, 235 and references cited therein. See also: Booth, B. L.; Hargreaves, R. G. *J. Chem. Soc. A* **1970**, 308.





48% yield. This reaction allows for the preparation of highly substituted butyrolactones by a direct "annulation" of an olefin—a reaction for which there is no equivalent in organic synthesis.

Alternatively, when **5** was stirred in methanol containing a catalytic amount of K_2CO_3, the keto ester **12** was isolated in modest (30%) yield. This reaction demonstrates that manganacycles such as **5** can also serve as precursors to 1,4-dicarbonyl systems via biscarbonylation of an olefin.

A single diastereomer of **11** was obtained from the reduction of **5** with $LiBEt_3H$; it was assigned the stereochemistry shown from ^1H NMR spectroscopy. The proton H-3 appears as a broad singlet at δ 2.43, width at half-height of 8 Hz. Irradiation of the bridgehead proton, H-6, results in sharpening of the H-3 signal into a doublet with J = 6.7 Hz: H-3 must be endo and syn to H-4. Therefore, we propose that **5** arises from syn addition of the acylmanganese moiety onto the exo face of norbornylene.

In conclusion, it has been demonstrated that high-pressure techniques are useful in the preparation of manganacycles **5**–**7** from the reaction of alkylmanganese pentacarbonyl complexes and olefins and that complexes **5**–**7** can be readily converted into butyrolactones and 1,4-dicarbonyl compounds.

Acknowledgment. We acknowledge the financial support of the National Institutes of Health (GM 30743) and numerous helpful discussions with Professors G. Geoffroy and A. Sen of this department. Partial support for the purchase of a Bruker WP-200 NMR spectrometer from the National Science Foundation is also acknowledged.

Registry No. **1** (R = Me), 13601-24-6; **1** (R = CH_2Ph), 14049-86-6; **5**, 88996-56-9; **6**, 88996-57-0; **7**, 89016-71-7; **8**, 13963-91-2; **9**, 14058-20-9; **10**, 88996-58-1; **11**, 89063-56-9; **12**, 88996-59-2; CO, 630-08-0; $LiBEt_3H$, 22560-16-3; K_2CO_3, 584-08-7; $P(OCH_3)_3$, 121-45-9; norbornylene, 498-66-8; cyclopentene, 142-29-0.

Supplementary Material Available: Spectroscopic data (^1H NMR, ^{13}C NMR, IR, mass spectral) for the compounds reported (7 pages). Ordering information is given on any current masthead page.

Halocarbon Binding in $[Ir(cod)(\eta^2\text{-}o\text{-}BrC_6H_4PPh_2)]SbF_6$

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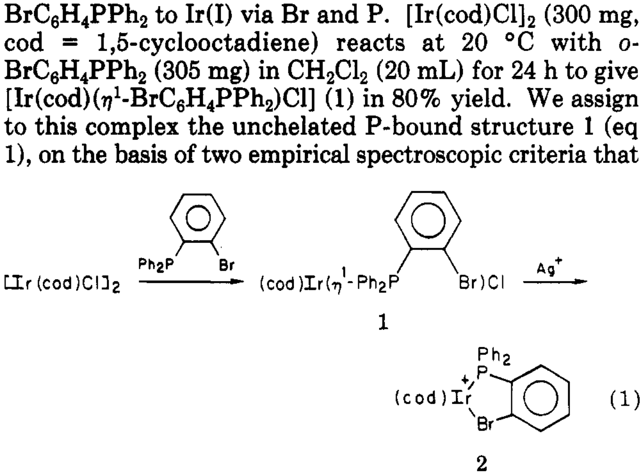
Summary: In the complex $[Ir(cod)(\eta^2\text{-}L)]SbF_6$ (**2**, L = o-$BrC_6H_4PPh_2$), L chelates to Ir via P and the Br bound to the aromatic ring. Complex **2** was formed from $Ir(cod)(\eta^1\text{-}L)Cl$ (**1**) with $AgSbF_6$. **2** reacts with Cl^- to give **1**, with MeCN to give $[Ir(cod)(MeCN)(\eta^1\text{-}L)]SbF_6$ reversibly, and with H_2 to give $[IrH_2(cod)(\eta^2\text{-}L)]SbF_6$, a hydrogenation catalyst.

We recently showed[3] that intact halocarbons such as o-$C_6H_4X_2$ (X = Cl, Br, I) or MeI can bind to transition metals via X to give complexes in which X plays the role of a neutral 2e donor, much like P in PR_3 or S in SR_2 complexes. Although the formation of halocarbon complexes had previously been proposed,[4] no definitive crystallographic evidence was obtained to support these formulations.

We wondered why our halocarbon complexes were stable and did not undergo oxidative addition. Since all our examples had involved Ir(III), it could be argued that oxidation to Ir(V) might be unfavorable. We therefore decided to try to make Ir(I) halocarbon complexes because this argument would not then apply, oxidative addition to Ir(I) to give Ir(III) being commonplace.[5] This paper describes preliminary results on the chelation of o-$BrC_6H_4PPh_2$ to Ir(I) via Br and P. $[Ir(cod)Cl]_2$ (300 mg, cod = 1,5-cyclooctadiene) reacts at 20 °C with o-$BrC_6H_4PPh_2$ (305 mg) in CH_2Cl_2 (20 mL) for 24 h to give $[Ir(cod)(\eta^1\text{-}BrC_6H_4PPh_2)Cl]$ (**1**) in 80% yield. We assign to this complex the unchelated P-bound structure **1** (eq 1), on the basis of two empirical spectroscopic criteria that have emerged from our work (see below). In chelated systems, the ^{31}P NMR resonance of the phosphorus nucleus lies at δ +45–60 (ppm to low field of external H_3PO_4); in unchelated ones it lies at δ +15–30. Entirely analogous findings for chelating diphosphines have been reviewed by Garrou.[6a] In the case of five-membered chelate di-



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(1) Yale University.

(2) Oklahoma State University.

(3) (a) Crabtree, R. H.; Faller, J. W.; Mellea, M. F.; Quirk, J. M. *Organometallics* **1982**, *1*, 1361. (b) Crabtree, R. H.; Mellea, M. F.; Quirk, J. M. *J. Chem. Soc., Chem. Commun.* **1981**, 1217.

(4) (a) Lawson, D. N.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1733. (b) A crystallographic study[4c] failed to support the binding of MeI proposed in ref 4a. (c) Troughton, P. G. H.; Skapski, A. C. *J. Chem. Soc., Chem. Commun.* **1968**, 575. (d) Beck, W.; Schloter, K. *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **1978**, *33B*, 1214.

(5) Vaska, L., *Acc. Chem. Res.* **1968**, *1*, 335.

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