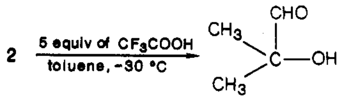

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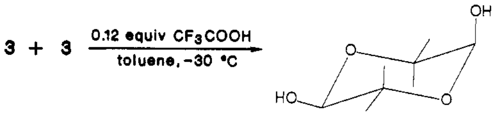

(4)

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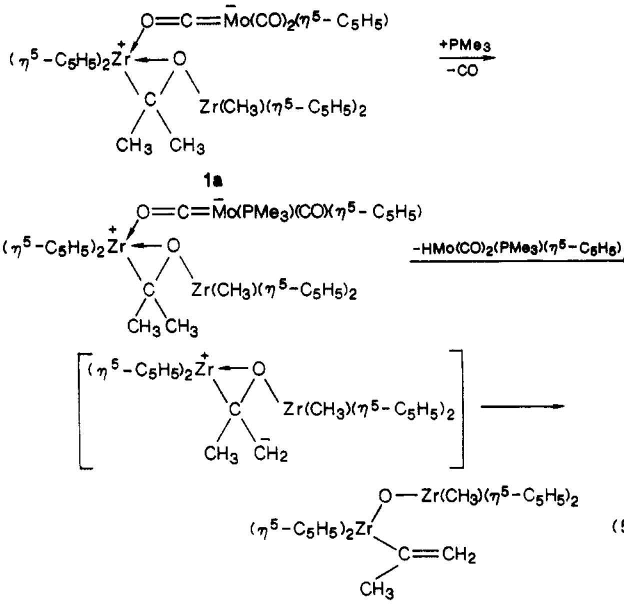
The formation of 3 by the acidification of 2 completes the stoichiometric hydroformylation of the coordinated acetone in 1. In contrast to the ketone ligands in mononuclear Zr complexes,[5] the acetone ligand in 1 is surprisingly unreactive toward potential insertion reagents other than CO: ethylene, butadiene, and cyclopentadiene do not react with 1 in toluene solution at room temperature; diphenylacetylene and 1 do not react in toluene at room temperature and decompose at 70 °C. Also in contrast to the ketone ligands in mononuclear Zr complexes,[16] the acetone ligand in 1 does not react with MeI. The addition of PMe_3 to 1a (toluene, 50 °C) leads to formation of an oxo-bridged dimer with a vinyl ligand on one zirconium (5),[17] presumably by substitution on Mo,[18] deprotonation of the acetone by the resulting strongly basic molybdenum anion, and C–O bond cleavage of the enolate thereby formed (eq 5). The same product is formed when 1a is treated with $K[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PMe_3)]$ performed from KH and $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PMe_3)H$. As the carbonyl of 1 is derived from CO, reaction 5 finishes a stoichiometric cleavage of the CO triple bond. The structure of 5 has been confirmed by observing the formation of propene upon its acidification with CF_3COOH.



(5)

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Acknowledgment. We thank the National Science Foundation for support by Grant CHE-8516415 and M. M. Miller for assistance with the preparation of this paper. The X-ray diffractometer and computer system were purchased with the support of the National Science Foundation.

Supplementary Material Available: Atomic coordinates and isotropic thermal parameters (Table S-2), bond lengths (Table S-3), bond angles (Table S-4), anisotropic thermal parameters (Table S-5), and hydrogen coordinates and thermal parameters (Table S-6) for **2b** (8 pages); observed and calculated structure factors for **2b** (Table S-1, 18 pages). Ordering information is given on any current masthead page.

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[14] To our surprise, the axial–equatorial isomer shown for 4 (the only isomer with four inequivalent methyl groups) appears to be the most stable dimer of 3; heating a solution of 4 only regenerates 3. Apparently the geometry of 4 is a compromise between the diaxial hydroxyls expected on electronic grounds (the anomeric effect[15]) and the diequatorial hydroxyls expected on steric grounds.

[15] Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon: New York, 1983; p 5.

[16] Erker, G.; Rosenfeldt, F. *Tetrahedron* **1982**, *38*, 1285.

[17] The ^1H NMR (C_6D_6) of **5**: δ 6.02 (d of q, $^2J_{HH} = 4.2$ Hz, $^4J_{HH} = 1.2$ Hz, 1 H vinyl), 5.81 (s, 10 H, Cp_2Zr), 5.77 (s, 10 H, Cp_2Zr), 5.26 (d of q, $^2J_{HH} = 4.2$ Hz, $^4J_{HH} = 1.2$ Hz, 1 H, vinyl), 2.09 (t, $^4J_{HH} = 1.2$ Hz, 3 H, $ZrCMe{=}CH_2$), 0.27 (s, 3 H, ZrMe). IR (KBr): 1434.5 (C=C), 1011, 884, 800, 733.5 (Zr–O–Zr) cm^{-1}. Anal. ($C_{24}H_{28}OZr_2$) C, H.

[18] Lewis acid cations are known to labilize $[CpMo(CO)_3]^-$: Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521.

Metal Vapor Synthesis of Bis(arene)manganese Cations Utilizing in Situ Oxidation

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Summary: The cocondensation of Mn atoms, I_2, and arenes at −196 °C provides a general route to homoleptic 18-electron $(\eta^6\text{-arene})_2Mn^+$ sandwich complexes. The reaction presumably involves in situ oxidation of unstable 19-electron $(\eta^6\text{-arene})_2Mn$ species.

Metal vapor synthesis has proven to be a valuable synthetic technique in the organometallic chemistry of many transition metals.[1] Manganese appears to be an exception as there are few references to manganese atom chemistry[2] and low yields are generally found in reactions which lead to organomanganese products.[2,3] Among the postulates presented for the source of the low yields is the tendency for manganese atoms to react with themselves rather than with organic ligands, possibly because of the stability of the half-filled 3d shell in the Mn ground state.[2] A more compelling explanation may be the instability of the Mn(0) odd-electron intermediates which would typically be formed in reactions of Mn atoms with organic ligands. This communication describes the trapping of such intermediates by cocondensation of an oxidant with arenes and manganese atoms; a series of new bis(arene)manganese cations is obtained.

A bell-jar metal reactor[4] was designed which incorporated a resistively heated furnace and a dual ligand inlet system. Cocondensation of manganese metal, toluene, and elemental iodine yielded $(\eta^6\text{-}C_6H_5CH_3)_2Mn^+PF_6^-$ (**1a**) on

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[1] (a) Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academic: New York, 1980. (b) Blackborow, J. R.; Young, D. *Metal Vapour Synthesis in Organometallic Chemistry*; Springer-Verlag: Berlin, 1979.

[2] Kündig, E. P.;Timms, P. L.; Kelly, B. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 901.

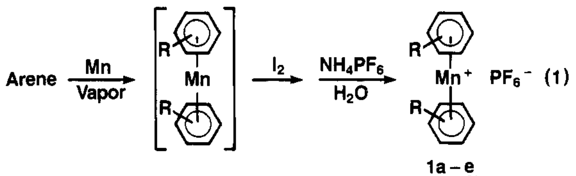
[3] Green, M. L. H.; O'Hare, D.; Wallis, J. M. *J. Chem. Soc., Chem. Commun.* **1984**, 233.

[4] Green, M. L. H. *J. Organomet. Chem.* **1980**, *200*, 119.

workup and ion exchange.[5] Similar reactions with *o*-, *m*-, and *p*-xylene and mesitylene also yielded the corresponding (η^6-arene)$_2$Mn$^+$PF$_6^-$ complexes (**1b–e**). The bis(arene)manganese cations may be isolated as their I$^-$ salts, but these are considerably less stable than the hexafluorophosphate salts. We have been unable to isolate a stable (η^6-C$_6$H$_6$)$_2$Mn$^+$ complex. The (η^6-arene)$_2$Mn$^+$PF$_6^-$ complexes are soluble in polar organic solvents and are stable in these solvents in the absence of air and light. The crystalline solids may be handled in air for short periods of time. Upon decomposition, the (η^6-arene)$_2$Mn$^+$PF$_6^-$ complexes release the free arene ligand.

The new complexes **1a–e** have been thoroughly characterized; ^{1}H and ^{13}C NMR and FAB MS data clearly support their formulation as cationic bis(arene) sandwich compounds.[6] To the best of our knowledge, the only other documented (η^6-arene)$_2$Mn$^+$ complex is (η^6-C$_6$H$_6$)Mn(η^6-C$_6$(CH$_3$)$_6$)$^+$PF$_6^-$ which was isolated in 2% yield from the cyclotrimerization of 2-butyne by (C$_6$H$_5$)$_2$Mn.[7] The properties of **1a–e** are in good agreement with those reported for (η^6-C$_6$H$_6$)Mn(η^6-C$_6$(CH$_3$)$_6$)$^+$PF$_6^-$.[7]

In the absence of I$_2$, we are unable to isolate any Mn-containing organometallic species from the condensation of Mn atoms and arenes. Dark gray to black matrices are observed which yield finely divided Mn metal on warmup; similar results have been reported by other laboratories.[8] This may be taken as good evidence that incorporation of I$_2$ into the reaction matrix traps an unstable intermediate. We thus envision the formation of **1a–e** proceeding via an unstable 19-electron sandwich complex which is oxidized by I$_2$ in the reaction matrix to yield the observed 18-electron (η^6-arene)$_2$Mn$^+$ complex (eq 1). Precedent for such an oxidation exists in the well-known reaction of (η^6-arene)$_2$Cr complexes with I$_2$ to form the 17-electron (η^6-arene)$_2$Cr$^+$ complexes.[9] The presence of I$_2$ does create a potential problem in that it may compete with arene for



1a–e

Arene = toluene (**1a**), o-xylene (**1b**), m-xylene (**1c**), p-xylene (**1d**), mesitylene (**1e**)

Mn atoms by forming MnI$_2$; reactor design and control over reactant ratios should minimize this problem.

In conclusion, we have successfully demonstrated the use of in situ oxidations in metal vapor synthesis. The preparation of (η^6-arene)$_2$Mn$^+$ complexes from the reaction of Mn atoms, arenes, and iodine lends support to the postulate that the low yields typically observed in the reactions of Mn atoms with organic ligands[2,3] are related to the instability of the 19-electron Mn(0) intermediates formed. Although the overall yields of (η^6-arene)$_2$Mn$^+$ complexes are disppointingly low (1–2%, based on I$_2$ or Mn), significant amounts may be obtained in a single run. Thus, a series of homoleptic (η^6-arene)$_2$Mn$^+$ complexes are, for the first time, available in quantities that will allow elucidation of their chemcal and physical properties.

Acknowledgment is made to the 3M Company by W.E.B. for its generous research support.

Registry No. **1a**, 116301-18-9; **1b**, 116301-20-3; **1c**, 116301-22-5; **1d**, 116301-24-7; **1e**, 116301-26-9; Mn, 7439-96-5.

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(5) **Synthesis of 1a.** All manipulations were performed under inert-atmosphere conditions. Manganese metal (3.72 g, 67.7 mmol), iodine (3.45 g, 27.2 mmol), and toluene (180 mL, 1.69 mol) were cocondensed at −196 °C over a 2-h period. The reactor was warmed to room temperature, vented with nitrogen, and the reaction mixture was syphoned into a Schlenk flask. The reactor walls were washed with THF; the reaction mixture and THF washes were filtered through Celite and evaporated to dryness under vacuum. The residue was dissolved in 25 mL of acetone and filtered into 30 mL of water containing 0.25 g of ammonium hexafluorophosphate. A pink precipitate formed and was collected by filtration. The precipitate was dissolved in 15 mL of THF, and the solution was cooled to −15 °C to afford (η^6-C$_6$H$_5$CH$_3$)$_2$Mn$^+$PF$_6^-$ (0.11 g, 0.286 mmol, 1.0% based on iodine) as orange-pink crystals.

(6) **Characterization of 1a**: ^{1}H NMR (90 MHz, acetone-d_6, δ) 5.74 (br s, C$_6$*H*$_5$CH$_3$), 2.39 (s, C$_6$H$_5$C*H*$_3$); ^{13}C{^{1}H} NMR (22.5 MHz, acetone-d_6, ppm) 98.1, 84.2, 83.2, and 82.3 (s, 1:2:2:1, *C*$_6$H$_5$CH$_3$), 19.4 (s, C$_6$H$_5$*C*H$_3$); FAB MS, *m/z* (relative intensity) 240 ([M + H]$^+$, 17), 239 ([M]$^+$, 100), 147 ([M − C$_6$H$_5$CH$_3$]$^+$, 15). Anal. Calcd for C$_{14}$H$_{16}$F$_6$MnP: C, 43.77; H, 4.20. Found: C, 43.60; H, 3.87. **1b**: ^{1}H NMR (90 MHz, acetone-d_6, δ) 5.68 (d, *o*-C$_6$*H*$_4$(CH$_3$)$_2$), 2.42 (s, *o*-C$_6$H$_4$(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (22.5 MHz, acetone-d_6, ppm) 97.9, 85.7, and 83.9 (s, 2:2:2, *o*-*C*$_6$H$_4$(CH$_3$)$_2$), 18.1 (s, *o*-C$_6$H$_4$(*C*H$_3$)$_2$); FAB MS, *m/z* (relative intensity) 267 ([M]$^+$, 100%). **1c**: ^{1}H NMR (90 MHz, acetone-d_6, δ) 5.63 (s, *m*-C$_6$*H*$_4$(CH$_3$)$_2$), 2.42 (s, *m*-C$_6$H$_4$(C*H*$_3$)$_2$); ^{13}C{^{1}H} (22.5 MHz, acetone-d_6, ppm) 98.9, 86.1, and 84.1 (s, 2:1:3, *m*-*C*$_6$H$_4$(CH$_3$)$_2$), 19.8 (s, *m*-C$_6$H$_4$(*C*H$_3$)$_2$); FAB MS, *m/z* (relative intensity) 268 ([M + H]$^+$, 25), 267 ([M]$^+$, 100), 161 ([M − C$_8$H$_{10}$]$^+$, 23). **1d**: ^{1}H NMR (90 MHz, acetone-d_6, δ) 5.62 (s, *p*-C$_6$*H*$_4$(CH$_3$)$_2$), 2.42 (s, *p*-C$_6$H$_4$(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (22.5 MHz, acetone-d_6, ppm) 97.9 and 85.1 (s, 2:4, *p*-*C*$_6$H$_4$(CH$_3$)$_2$), 19.3 (s, *p*-C$_6$H$_4$(*C*H$_3$)$_2$); FAB MS, *m/z* (relative intensity) 267 ([M]$^+$, 100). **1e**: ^{1}H NMR (90 MHz, acetone-d_6, δ) 5.42 (s, C$_6$*H*$_3$(CH$_3$)$_3$), 2.47 (s, C$_6$H$_3$(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR (22.5 MHz, acetone-d_6, ppm) 99.1 and 85.3 (s, 3:3, *C*$_6$H$_3$(CH$_3$)$_3$), 19.5 (s, C$_6$H$_3$(*C*H$_3$)$_3$); FAB MS, *m/z* (relative intensity) 296 ([M + H]$^+$, 100), 178 ([M − C$_9$H$_{10}$]$^+$, 29), 175 ([M − C$_9$H$_{12}$]$^+$, 33).

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(8) (a) Efner, H. F.; Tevault, D. E.; Fox, W. B.; Smardzewski, R. R. *J. Organomet. Chem.* **1978**, *146*, 45. (b) Klabunde, K. J.; Efner, H. F. *J. Fluorine Chem.* **1974**, *4*, 114.

(9) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, p 999.

Reactivity of Rh(PMe$_3$)$_4$Cl with Lithium Derivatives of Phosphorus-Substituted Diazomethanes. First Evidence for a Transient Nitrogen–Transition-Metal Nitrile Imine. X-ray Structure of (PMe$_3$)$_2$RhNBuNCHP(N-*i*-Pr$_2$)$_2$

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Summary: Reaction at the diazo carbon atom occurred when the lithium derivative of [bis(diisopropylamino)thioxophosphoranyl]diazomethane and Rh(PMe$_3$)$_4$Cl were allowed to react. The 16-electron Rh(I)–C bonded diazo complex (PMe$_3$)$_2$RhC(N$_2$)P(N-*i*-Pr$_2$)$_2$(S) (**1**) containing a rhodium–sulfur bond was obtained. In contrast, when the lithium derivative of [bis(diisopropylamino)phosphino]diazomethane was used, the reaction took place at the terminal diazo nitrogen atom. The formation of (PMe$_3$)$_2$RhN-*n*-BuNCHP(N-*i*-Pr$_2$)$_2$ (**2**) is explained by the transient formation of a nitrogen–rhodium nitrile imine.

We have recently found that the lithium derivative of (trimethylsilyl)diazomethane reacts with Rh(PMe$_3$)$_4$Cl to