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Synthesis and Reactivity of Metallacyclic Manganese α-(Silyloxy)alkyl Complexes (CO)$_4\overline{\mathrm{MnC(R)(OSi(CH_3)_3)P}}$(C$_6H_5$)$_2$. A New Thermodynamic Driving Force for CO Insertion

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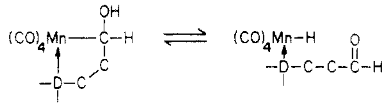
Reaction of (CO)$_5$MnR (**2**) with (C$_6$H$_5$)$_2$PSi(CH$_3$)$_3$ (**3**) gives metallacyclic α-(silyloxy)alkyl complexes (CO)$_4\overline{\mathrm{MnC(R)(OSi(CH_3)_3)P}}$(C$_6H_5$)$_2$ (**4**) in 42–75% yields (R = CH$_3$ (**a**), CH$_2$Si(CH$_3$)$_3$ (**b**), C$_6$H$_5$ (**c**), 2-naphthyl (**d**)). These reactions are of interest in that the metallacyclic carbon is derived from an "insertion" of CO into the manganese–carbon bond of **2**—a step for which subsequent silicon–oxygen bond formation provides an additional thermodynamic driving force. Reaction of (CO)$_5$MnCOC$_6$H$_5$ with **3** also gives **4c** (63%). Phosphines (C$_6$H$_5$)$_3$P and **3** react with **2a** at nearly the same rate, both separately and in competition experiments. Passage of **4b** through wet silica gel gives acyl complex *cis*-(CO)$_4\overline{\mathrm{Mn(COCH_2Si(CH_3)_3)P}}$(C$_6H_5$)$_2$H (**6b**, 84%), presumably via metallacyclic α-hydroxyalkyl complex (CO)$_4\overline{\mathrm{MnC(CH_2Si(CH_3)_3)(OH)P}}$(C$_6H_5$)$_2$ (**7b**). Reaction of **2b** with (C$_6$H$_5$)$_2$PH also gives **6b** (91%). Reaction of (CO)$_5$MnH and **3** in hexanes gives *cis*-(CO)$_4$Mn(H)P(C$_6$H$_5$)$_2$Si(CH$_3$)$_3$ (**8**, 72%). Both **8** and **4a** are inert to 300–360 psi of CO. The thermodynamics of these transformations are analyzed.

Introduction

In the two previous papers,[1,2] we have carefully examined the stability of metallacyclic manganese α-hydroxyalkyl complexes containing a five-membered ring (**1**) with respect to the equilibrium shown in eq 1. Depending upon the nature of the donor atom D and the bridging carbons, K_{eq} of both >>1 and <<1 were found. We sought to study the effect of metallacycle size upon this equilibrium.



(1)

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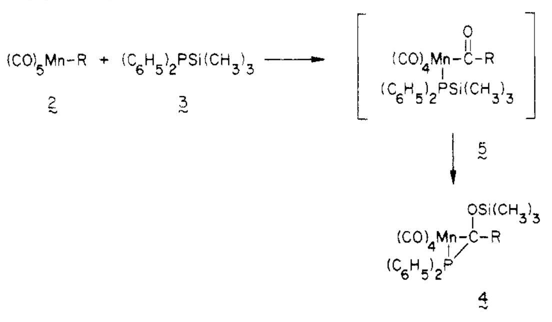
Several synthetic approaches to four-membered analogues of metallacycle **1** were unsuccessful.[2] Hence, we sought preparative routes to three-membered analogues of **1**. In this paper, we report that manganese complexes (CO)$_5$MnR (**2**, R = alkyl, aryl) and the silylated phosphine (C$_6$H$_5$)$_2$PSi(CH$_3$)$_3$ (**3**)[3] react to give metallacyclic manganese α-(silyloxy)alkyl complexes (CO)$_4\overline{\mathrm{MnC(R)(OSi(CH_3)_3)P}}$(C$_6H_5$)$_2$ (**4**), as shown in eq 2. This reaction is of special interest in that the metallacyclic carbon is derived from an "insertion" of coordinated CO—a step for which subsequent silicon–oxygen bond formation provides an additional thermodynamic driving force. Complexes **4** can be used to generate α-hydroxyalkyl intermediates that prove unstable with respect to a new type of ring opening equilibrium. A portion of this study has been communicated.[4]



(2)

a, R = CH$_3$, 75%
b, R = CH$_2$Si(CH$_3$)$_3$, 52%
c, R = C$_6$H$_5$, 67%
d, R = 2-naphthyl, 42%

Results

Phosphines PR$_3$ commonly react with manganese alkyl complexes (CO)$_5$MnR (R = alkyl, aryl) to give acyl complexes (CO)$_4$Mn(COR)PR$_3$.[5] Hence, we treated methyl complex (CO)$_5$MnCH$_3$ (**2a**) with (C$_6$H$_5$)$_2$PSi(CH$_3$)$_3$ (**3**) in CH$_2$Cl$_2$. A product, **4a**, cleanly formed over the course of 12 h and was subsequently isolated in 75% yield. However, this product was not the acetyl complex (CO)$_4$Mn(COCH$_3$)P(C$_6$H$_5$)$_2$Si(CH$_3$)$_3$ (**5a**), as evidenced by the absence of an IR $\nu_{\mathrm{C=O}}$ (1550–1650 cm^{-1}) and an acyl carbon ^{13}C NMR resonance. Complex **4a** was assigned the metallacyclic structure (CO)$_4\overline{\mathrm{MnC(CH_3)(OSi(CH_3)_3)P}}$(C$_6H_5$)$_2$ (eq 2) based upon the spectroscopic data summarized in Tables I and II. Key features included IR $\nu_{\mathrm{C\equiv O}}$ and ^{13}C NMR CO resonance patterns characteristic of *cis*-(CO)$_4$MnLL′ complexes,[1,2] a Si(CH$_3$)$_3$ ^{1}H NMR chemical shift characteristic of oxygen-bound silicon and a ^{31}P NMR chemical shift close to that of metallacycle (CO)$_4\overline{\mathrm{MnCH_2P}}$(C$_6H_5$)$_2$ (13.0 ppm).[6] This latter compound had been prepared by Lindner from the reaction of [(CO)$_4$MnP(C$_6$H$_5$)$_2$]$^{2-}$ with CH$_2$Cl$_2$ and characterized by X-ray crystallography.[6] Numerous L$_n\overline{\mathrm{MCH_2P}}R_2$ complexes have been synthesized previously and are commonly referred to as ylide complexes.[7,8]

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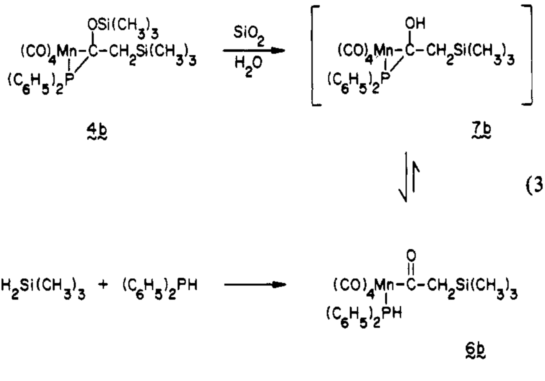
The scope of this unusual reaction was tested with additional substrates. Complex $(CO)_5MnCH_2Si(CH_3)_3$ (**2b**) and **3** reacted readily in benzene (2.5 h) to give metallacycle $(CO)_4\overline{MnC(CH_2Si(CH_3)_3)(OSi(CH_3)_3)P}(C_6H_5)_2$ (**4b**) in 52% yield after workup. Phenyl complex $(CO)_5MnC_6H_5$ (**2c**) and β-naphthyl complex $(CO)_5Mn(2\text{-}C_{10}H_7)$ (**2d**) were somewhat less reactive toward **3**, but metallacycles **4c** and **4d** (eq 2) were obtained in good yield in refluxing benzene. Benzyl complex $(CO)_5MnCH_2C_6H_5$ and **3** reacted in refluxing benzene to give a mixture of products which were not completely characterized: one of these appeared to be a metallacycle from its IR spectrum. Complexes of the type $(CO)_4Mn(COR)P(C_6H_5)_2Si(CH_3)_3$ (**5**) were not detected in any of these reactions.

Phosphine **3** also readily converted benzoyl complex $(CO)_5MnCOC_6H_5$ to metallacycle **4c** (benzene, 40 °C, 14 h, 63%). In side-by-side experiments (40 °C, identical reactant concentrations) the rate of this reaction was observed to be ca. three times that of **3** with phenyl complex **2c**.

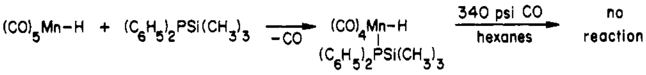
In order to help clarify the role of the $-Si(CH_3)_3$ substituent in the reaction of $(CO)_5MnCH_3$ (**2a**) with $(C_6H_5)_2PSi(CH_3)_3$ (**3**), the reaction of **2a** with $(C_6H_5)_3P$ was examined under identical conditions. The $t_{1/2}$ for the disappearance of **2a** were ca. 2.2 h (**3**) and 2.5 h ($(C_6H_5)_3P$). In the latter reaction, the previously reported products[9] *cis*- and *trans*-$(CO)_4Mn(COCH_3)P(C_6H_5)_3$ and *cis*-$(CO)_4Mn(CH_3)P(C_6H_5)_3$ formed. When an excess of $(C_6H_5)_2PSi(CH_3)_3$ (**3**) and $P(C_6H_5)_3$ (1:1) were allowed to compete for **2a**, ca. 1.1 times more **3** was consumed. This reactivity difference was misquoted in our communication.[4]

The feasibility of converting metallacyclic α-(silyloxy)alkyl complexes **4** into α-hydroxyalkyl complexes was probed next. Complex **4b** was passed through wet silica gel (eq 3). Subsequently, acyclic acyl complex *cis*-$(CO)_4Mn(COCH_2Si(CH_3)_3)P(C_6H_5)_2H$ (**6b**) was isolated in 84% yield. This reaction will be interpreted (Discussion) as proceeding through the metallacyclic α-hydroxyalkyl complex $(CO)_4\overline{MnC(CH_2Si(CH_3)_3)(OH)P}(C_6H_5)_2$ (**7b**). Complex **6b** was independently synthesized in 91% yield from alkyl complex **2b** and $(C_6H_5)_2PH$ (eq 3). Its structure followed readily from its spectroscopic properties (IR $\nu_{C=O}$; ^{13}C NMR acyl C=O resonance), as summarized in Tables I and II.



(3)

We sought to determine if **3** could effect CO insertion into a metal–hydrogen bond. Hence, $(CO)_5MnH$ and **3** were reacted under a variety of conditions. In hexanes, *cis*-$(CO)_4Mn(H)P(C_6H_5)_2Si(CH_3)_3$ (**8**) formed cleanly and was subsequently isolated in 72% yield (eq 4). In more polar solvents, varying amounts of $(CO)_5MnSi(CH_3)_3$ and *cis*-$(CO)_4Mn(H)P(C_6H_5)_2H$ (**9**) were also detected spectroscopically. An authentic sample of **9** was independently prepared (85% isolated) from the reaction of $(CO)_5MnH$ and $(C_6H_5)_2PH$.



$$(CO)_5Mn{-}H + (C_6H_5)_2PSi(CH_3)_3 \xrightarrow[-CO]{} \underset{(C_6H_5)_2PSi(CH_3)_3}{(CO)_4\overset{}{Mn}{-}H} \xrightarrow[\text{hexanes}]{\text{340 psi CO}} \text{no reaction}$$

3 8

(4)

In an attempt to force CO insertion, hydride complex **8** was treated with 340 psi of CO in hexanes at room temperature. No reaction was observed over the course of 3 days. In more polar solvents such as THF, CD_3CN, and acetone, decomposition occurred. Also, metallacycle **4a** was inert toward 300–360 psi of CO in benzene and CD_3CN.

Discussion

I. Synthesis of Metallacycles 4. The "insertion" of carbon monoxide into a metal–alkyl bond is a key step in many catalytic processes of industrial importance. Examples include olefin hydroformylation, methanol carbonylation, and the Reppe reaction.[10] Consequently, there is considerable interest in devising means of kinetically and/or thermodynamically promoting this reaction.

Recently, it has been shown that Lewis[11-13] and proton[13b,14] acids can greatly accelerate the insertion of CO into a metal–alkyl bond. Since in most cases the acid binds to the acyl complex product, but not to any significant degree to the starting alkyl complex, the insertion is thermodynamically driven as well. A representative example is given in eq 5.[12a] Phosphine ligands participate in many CO insertion reactions. Hence, phosphine ligands containing Lewis acid sites, or "amphoteric" phosphines, have also received recent attention.[15,16] Such ligands (e.g., $(C_6H_5)_2PN(t\text{-}C_4H_9)AlR_2$) can rapidly effect bond formation between coordinated CO and alkyl or hydride ligands. However, they also become irreversibly attached to the new ligand, and in some cases fundamentally new insertion mechanisms are likely involved. An example of such a reaction is given in eq 6.[15b] Finally, oxidizing agents have

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[8] See, inter alia, the following recent references: (a) Karsch, H. H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 921. (b) Karsch, H. H.; Neugebauer, D. *Ibid.* **1982**, *21*, 312. (c) Karsch, H. H. *Chem. Ber.* **1984**, *117*, 783. (d) Werner, H.; Gotzig, J. *Organometallics* **1983**, *2*, 547. (e) Mainz, V. V.; Andersen, R. A. *Organometallics* **1984**, *3*, 675. (f) Lindner, E.; Küster, E. U.; Hiller, W.; Fawzi, R. *Chem. Ber.* **1984**, *117*, 127. (g) Gibson, V. C.; Graimann, C. E.; Hare, P. M.; Green, M. L. H.; Brandy, J. A.; Grebenik, P. D.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1985**, 2025.

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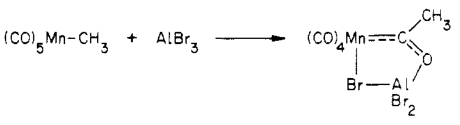
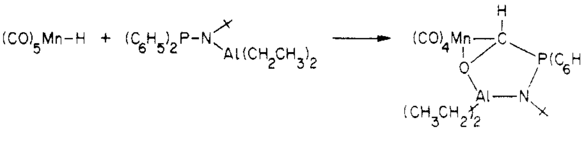
also been shown to catalyze CO insertion reactions.[17]


(5)


(6)

Phosphine **3** can also be considered an amphoteric ligand. In its reactions with manganese alkyl complexes $(CO)_5MnR$ (**2**), acyl complex **5** (eq 2) is likely initially formed. The basic acyl oxygen then abstracts the acidic $-Si(CH_3)_3$ group, with concomitant metallacycle (**4**) formation. Alternatively, the acyl C=O can be viewed as undergoing a 1,2-addition to the phosphorus–silicon bond. The 1,2-addition of $X-Si(CH_3)_3$ compounds to carbonyl groups is common.[18] Furthermore, Satgé and co-workers have previously observed the addition of $R_2P-SiR'_3$ compounds to acyl silanes.[18b] These reactions are generally considered to be driven by the formation of strong (106–127 kcal/mol)[19] silicon–oxygen bonds. We know of no other well-defined 1,2-addition reactions to metal acyl ligands.

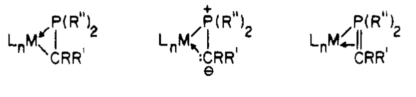
A phosphorus–carbon bond is also formed in the conversion **4** → **5**, and a carbon–oxygen π bond and a phosphorus–silicon σ bond are broken. Bond strengths for unstrained primary phosphorus–carbon bonds in phosphines are 62–67 kcal/mol.[20] It is difficult to estimate the strengths of the bonds that are broken, but plausible values would be 90 kcal/mol (C=O π)[21] and 51 kcal/mol (P—Si),[22] respectively.

As discussed in the previous paper,[2] the formation of complexes such as **5** proceeds via phosphine attack upon coordinatively unsaturated precursors of the type $(CO)_4Mn(COR)(S)$ (S = solvent or vacant coordination site).[5] Phosphines $(C_6H_5)_2PSi(CH_3)_3$ (**3**) and $(C_6H_5)_3P$ react with **2a** at virtually identical rates, both in competition experiments and separately. Hence, the $Si(CH_3)_3$ substituent in phosphine **3** does not kinetically promote any step of the CO insertion process. Intermediate $(CO)_4Mn(COR)(S)$ can also readily be generated by CO dissociation from acyl complexes $(CO)_5MnCOR$. This is likely the initial step in the formation of metallacycle **4c** from **3** and benzoyl complex $(CO)_5Mn(COC_6H_5)$.

Only one example of a CO insertion into a metal hydride bond to give a η^1-formyl complex, $L_nMH + CO \rightarrow L_nMCHO$, has been observed to date.[23] There is also good evidence that the insertion reaction $(CO)_5MnH + L \rightarrow (CO)_4Mn(CHO)L$ is uphill thermodynamically.[24,25] Hence, we were particularly interested in the outcome of the reactions shown in eq 4. On the basis of these results, it appears that silicon–oxygen bond formation is not a sufficient driving force to promote CO insertion into the manganese–hydrogen bond of **8**. This can be ascribed to the fact that manganese–hydrogen bonds are 20–30 kcal stronger than corresponding manganese–alkyl bonds.[25,26]

Previously, Haszeldine and co-workers reported that *cis*-$(CO)_4Mn(C_6H_5)P(C_6H_5)_3$ was the only isolable product from the reaction of $(CO)_5MnC_6H_5$ (**2c**) with $(C_6H_5)_3P$, although possible spectroscopic evidence for $(CO)_4Mn(COC_6H_5)P(C_6H_5)_3$ ($\nu_{C=O}$ = 1724 cm^{-1}?) was noted.[27] The reaction of **2c** with **3** to give **4c** (eq 2) demonstrates that **3** can in fact be used to trap CO insertion products which are kinetically and/or thermodynamically unstable.

II. Properties of Metallacycles 4. The nature of bonding in metallacycles of the type $L_n\overline{MC(R)(R')P}(R'')_2$ has been extensively studied and debated.[6-8] At least three types of resonance forms, A, B, and C, can be drawn. X-ray data have been interpreted as indicating a shorter than normal phosphorus–carbon bond length and hence a major contribution by C.[6,8b,f] The important conclusion for our purposes is that the bonding in complexes **4** is substantially different from that in larger ring metallacycles. Thus, the apparent inability of complexes **4** to carbonylate (which would likely decrease ring strain) can be rationalized.


A B C

Attempted generation of the metallacyclic α-hydroxyalkyl complex **7b** (eq 3) gives instead acyclic acyl complex **6b**. There are two thermodynamic factors which likely effect this ring opening. First, hydrogen–oxygen bonds in alcohols (ca. 104 kcal/mol)[28] are weaker than silicon–oxygen bonds. Second, phosphorus–hydrogen bonds (77 kcal/mol in PH_3)[20] are likely considerably stronger than phosphorus–silicon bonds. Thus, the factors that favor metallacycle formation in eq 2 are attenuated in eq 3.

Equation 3 also constitutes a new mode of ring opening for metallacyclic α-hydroxyalkyl complexes. The two options are summarized schematically in eq 7. Equation 3 is equivalent to path b in eq 7. In the previous papers[1,2] only equilibria of the type a (e.g., eq 1) were observed. We

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[23] (a) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 700. (b) Important related examples are the reactions of $(\eta^5\text{-}C_5Me_5)_2Th(OR)(H)$ complexes with CO to give η^2-formyl complexes $(\eta^5\text{-}C_5Me_5)_2\overline{Th(OR)=C(H)O}$. These reactions are driven by a Lewis acid–base interaction between the thorium and formyl oxygen: Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959.

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[26] The formation of $(CO)_5MnSi(CH_3)_3$ and complexes of $(C_6H_5)_2PH$ in reactions of $(CO)_5MnH$ and **3** in polar solvents likely occur via the ion pair $(CO)_5Mn^-[(C_6H_5)_2P(H)Si(CH_3)_3]^+$, followed by $Si(CH_3)_3$ transfer from phosphorus to manganese.

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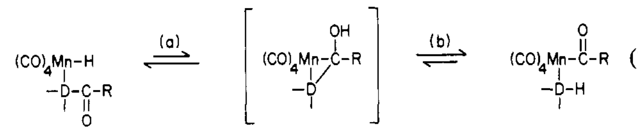

(7)

propose that path b will be favored when (1) the donor atom D (or other heteroatom) is directly bound to the α-hydroxyalkyl carbon and (2) the sum of the D–hydrogen and manganese–acyl bond strengths is greater than the sum of the D–acyl and manganese–hydrogen bond strengths. Manganese–acyl bonds are substantially *weaker* than manganese–hydrogen bonds.[25] Therefore (assuming eq 3 to be under thermodynamic control), phosphorus–hydrogen bonds of the type in **6b** must be substantially stronger than phosphorus–acyl bonds.

III. Summary and Relevance to Catalysis. We have developed a useful and distinctly new strategy for the synthesis of metallacyclic ylide complexes. The three-membered metallacycles thus prepared contain an α-(trimethylsilyl)oxy substituent and can therefore be used as precursors to α-hydroxyalkyl complexes. The latter prove unstable with respect to ring opening (eq 7, path b), thereby providing further support for the hemiacetal model for α-hydroxyalkyl complex behavior described in the previous papers.[1,2]

The insertion of CO into a metal–alkyl or metal–hydrogen bond is a key step in many homogeneously catalyzed CO/H_2 reactions.[10,29] The 1,2-addition of a phosphorus–silicon bond to the intermediate **5** in eq 2 provides an additional thermodynamic driving force for CO insertion. Unfortunately, the resulting complexes **4** appear to be inert toward further CO insertion, which would give a four-membered metallacycle. We speculate that it may be possible to prepare a functionalized phosphine, $(C_6H_5)_2P–X–Y$, where the X–Y bond can reversibly add to the acyl ligand in a *cis*-$(CO)_4Mn(COR)P(C_6H_5)_2XY$ intermediate. Since this would give a four-membered metallacycle, additional CO insertion might be possible. Such ligands may therefore alter and/or improve the selectivities of homogeneous catalysts for CO reduction.

Experimental Section

General Data and Solvents. General procedures employed were identical with those given in the previous papers.[1,2] Cyclohexane (Aldrich) was distilled from $LiAlH_4$ before use. All other solvents were purified as described in the previous papers.[1,2]

Reagents. Manganese complexes $(CO)_5MnCH_3$ (**2a**)[30] and $(CO)_5MnCOC_6H_5$[31] were prepared following literature procedures, except that isolated $K^+(CO)_5Mn^-$ (from $Mn_2(CO)_{10}/NaK_{2.8}/$ether)[32] was used. Complex $(CO)_5MnC_6H_5$ (**2c**)[31] was prepared from C_6H_5COCl and isolated $K^+(CO)_5Mn^-$ in refluxing THF analogously to **2d** below. Complex $(CO)_5MnBr$ was prepared by a literature procedure.[33]

Phosphine $(C_6H_5)_2PH$ (Strem) and silane $(CH_3)_3SiCH_2Cl$ (Petrarch) were used as received. Reagent 2-naphthoyl chloride was prepared by a literature procedure.[34] Lithium powder (1% Na) in mineral oil (Alfa) was washed with hexanes (glovebox) and vacuum dried before use. All other reagents were obtained as described in the previous papers.[1,2]

Synthesis of $(C_6H_5)_2PSi(CH_3)_3$ (3).[35] In a typical experiment, a Schlenk flask was charged with Li wire (ca. 0.4 g, 58 mmol), THF (90 mL), and $(C_6H_5)_2PCl$ (4.0 mL, 22 mmol). The reaction was stirred for 12 h, after which time the excess Li wire was removed by using forceps. This $(C_6H_5)_2PLi$ solution was cooled to −78 °C, and $(CH_3)_3SiCl$ (4.0 mL, 32 mmol) was then added. After a few minutes, the reaction was allowed to slowly warm to room temperature. The mixture was taken into a glovebox, and most of the THF was removed by rotary evaporation. Hexanes was added, and the resulting mixture was filtered through a fritted (M) funnel containing glass wool. Solvent was removed by rotary evaporation. The resulting liquid residue was distilled under oil pump vacuum (113 °C) to give **3** (5.2 g, 20 mmol, 91%) as a colorless liquid (^1H NMR (δ, C_6D_6) 0.13 (d, J = 4.7 Hz)), which was stored cold. Yields ranged from 83% to 91%.

Synthesis of $(CH_3)_3SiCH_2Li$.[36] A schlenk flask was charged with Li powder (1% Na, 0.117 g, 16.9 mmol) and cyclohexane (15 mL) under an argon atmosphere. This mixture was refluxed for 1 h. The flask was cooled, and then $(CH_3)_3SiCH_2Cl$ (1.0 mL, 7.2 mmol) was added. The solution was stirred for 1 h and then refluxed for an additional 1.25 h. The reaction was cooled, taken into a glovebox, and filtered through glass fiber filter paper. The filter paper was rinsed with hexanes. Solvent was removed from the filtrate by rotary evaporation. The resulting white residue was sublimed (100 °C, 10^{-5} torr) onto a water-cooled cold finger to give $(CH_3)_3SiCH_2Li$ (0.418 g, 4.4 mmol, 61%) as a white powder.

Synthesis of $(CO)_5MnCH_2Si(CH_3)_3$ (2b).[37] A Schlenk flask was charged with $(CO)_5MnBr$ (1.10 g, 4.0 mmol), THF (80 mL), and a magnetic stir bar. This mixture was cooled to −78 °C, and then a solution of $(CH_3)_3SiCH_2Li$ (0.418 g, 4.44 mmol) in ether (15 mL) was added dropwise. Stirring was continued for 0.5 h, after which the reaction mixture was allowed to slowly warm to room temperature. The reaction was transferred to a round-bottom flask (CH_2Cl_2 rinse), and solvent was removed by rotary evaporation under water aspirator vacuum (higher vacuum volatilized **2b**). The resulting residue was transferred to a glovebox and taken up in hexanes. This mixture was filtered through a fritted (M) funnel containing a plug of silica gel. About 150 mL of hexanes was used. The filtrate was taken out of the glovebox, and solvent was removed by rotary evaporation as described above. The residue was vacuum distilled (10^{-5} torr) by using a 14/20 short-path head and an ice bath-cooled receiver flask. This gave **2b** (0.706 g, 2.50 mmol, 63%) as a yellow liquid which must be stored cold. ^1H NMR (δ, CD_2Cl_2): 0.10 (s, 9 H), −0.59 (s, 2 H).

Synthesis of $(CO)_5Mn(2\text{-}C_{10}H_7)$ (2d; $2\text{-}C_{10}H_7$ = β-Naphthyl). A Schlenk flask was charged with $K^+(CO)_5Mn^-$ (0.531 g, 2.27 mmol), THF (30 mL), and a magnetic stir bar. The solution was stirred and 2-naphthoyl chloride (0.489 g, 2.57 mmol) in THF (5 mL) was added dropwise. Additional THF (15 mL) was added. The reaction was stirred for 0.5 h, refluxed for 2 h, allowed to cool, and subsequently worked up in air except when noted otherwise. Solvent was removed by room temperature rotary evaporation under water aspirator vacuum. The residue was taken up in CH_2Cl_2 and filtered through a plug of silica gel. Solvent was removed from the filtrate, and the residue was taken up in hexanes. This solution was applied to the top of 2 × 30 cm silica gel column which had been packed in hexanes. The column was eluted with hexanes. A yellow $Mn_2(CO)_{10}$ fraction was followed by a colorless product fraction. The latter was collected under a N_2 purge, and solvent was then removed by rotary evaporation. The resulting residue was sublimed (65 °C, oil pump vacuum) onto a water-cooled cold finger. White crystals of **2d** (0.482 g, 1.50 mmol, 66%) were collected; mp 71–72 °C (capillary sealed under N_2). IR (cm^{-1}, hexanes): 2115 m, 2021 vs, 2000 s ($\nu_{C≡O}$). ^1H NMR (δ, CD_2Cl_2): 7.98 (s, 1 H), 7.74–7.60 (m, 4 H), 7.44–7.32 (m, 2 H). ^{13}C NMR (ppm, CD_2Cl_2, −20 °C): 212.1 (cis CO), 210.6 (trans CO), naphthyl at 2 × 144.1, 142.3, 134.9, 131.9, 128.2, 127.4, 126.9, 126.6, 125.6. Mass spectrum (m/e (relative intensity), 70 eV): 322 (M^+, 10), 294 (M^+ − CO, 6), 266 (M^+ − 2CO, 14), 238 (M^+ − 3CO, 14), 210 (M^+ − 4CO, 11), 182 (M^+ − 5CO, 100). Anal. Calcd for $C_{15}H_7MnO_5$: C, 55.92; H, 2.19; Mn, 17.05. Found: C, 55.72; H, 2.21; Mn, 17.09.

Synthesis of $(CO)_4Mn\overline{C(CH_3)(OSi(CH_3)_3)P}(C_6H_5)_2$ (4a). A

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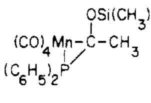
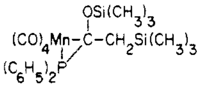
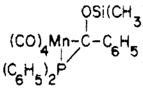
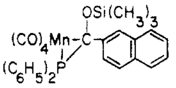
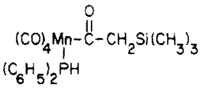
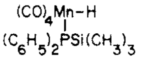
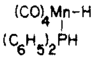
Table I. ^{1}H, ^{13}C, and ^{31}P NMR Data for New Organometallic Compounds

		^{13}C{^{1}H} NMR,[b–d] ppm			
compd	^{1}H NMR,[a] δ	CO	aryl	other	^{31}P{^{1}H} NMR,[e] ppm
 **4a**	8.00–7.80 (m, 4 H), 7.60–7.36 (m, 6 H), 2.14 (d, J_{HP} = 8.4 Hz, 3 H), 0.14 (s, 9 H)[f]	226.5 (s), 221.1 (d, J = 12.6 Hz),[c] 219.3 (d, J = 20.5 Hz), 216.9 (d, J = 15.6 Hz)[f]	*o*, 136.0 (d, J = 12.8 Hz),[c] 135.6 (d, J = 12.6 Hz); *p*, 133.1 (s), 132.4 (s); *i*, 131.9 (d, J = 48.6 Hz), 130.5 (d, J = 41.1 Hz); *m*, 130.5 (d, J = 12.6 Hz), 130.0 (d, J = 10.5 Hz)[f]	68.7 (d, J = 10.2 Hz, MnC),[c] 32.2 (s, CCH_3), 1.8 (s, SiC)[f]	7.91[f]
 **4b**	7.89–7.71 (m, 4 H), 7.56–7.41 (m, 6 H), 2.02 (dd, J_{HH} = 15.2 Hz, J_{HP} = 16.5 Hz, 1 H), 1.79 (dd, J_{HH} = 15.2 Hz, J_{HP} = 1.1 Hz, 1 H), 0.07 (s, 9 H), 0.03 (s, 9 H)	224.9 (s), 220.0 (br s), 218.9 (d, J = 16.6 Hz), 216.8 (d, J = 16.6 Hz)	*o*, 135.9 (d, J = 12.6 Hz), 135.1 (d, J = 11.5 Hz); *p*, 131.7 (s), 131.1 (s); *i*, 130.5 (d, J = 44.0 Hz), 129.3 (d, J = 37.4 Hz); *m*, 129.3 (d, J = 11.5 Hz), 129.0 (d, J = 11.5 Hz)	73.6 (d, J = 37.0 Hz, MnC), 36.2 (s, CH_2), 1.4 (s, SiC), 0.2 (s, SiC)	11.7
 **4c**	8.14–8.06 (m, 2 H), 7.73–7.70 (m, 2 H), 7.61–7.57 (m, 3 H), 7.45–7.21 (m, 8 H), −0.13 (s, 9 H)	225.0 (s), 219.5 (d, J = 12.9 Hz), 217.8 (d, J = 18.0 Hz), 214.8 (d, J = 17.8 Hz)	$P(C_6H_5)_2$: *o*, 135.6 (d, J = 10.4 Hz), 134.8 (d, J = 12.7 Hz); *p*, 131.4 (s), 131.1 (s); *i*, 130.1 (d, J = 49.0 Hz), 130.0 (d, J = 38.8 Hz); *m*, 129.0 (d, J = 12.6 Hz), 128.8 (d, J = 10.5 Hz). CC_6H_5: 142.9 (s), 134.3 (d, J = 7.2 Hz), 128.4 (s), 128.2 (s)	76.9 (d, J = 25.4 Hz, MnC), 0.5 (s, SiC)	5.93
 **4d**	8.16–8.02 (m, 3H), 7.89–7.77 (m, 4 H), 7.63–7.42 (m, 7 H), 7.30–7.16 (m, 3 H)	224.9 (s), 219.5 (d, J = 10.3 Hz), 217.7 (d, J = 17.9 Hz), 214.9 (d, J = 15.5 Hz)	$P(C_6H_5)_2$: *o*, 135.5 (d, J = 10.4 Hz), 134.7 (d, J = 10.6 Hz); *p*, 131.4 (s), 131.2 (s); *i*, 130.1 (d, J = 51.4 Hz), 129.9 (d, J = 38.7 Hz); *m*, 129.0 (d, J = 12.6 Hz), 128.7 (d, J = 12.7 Hz). $C_{10}H_7$: 141.1 (s), 133.2 (s), 132.8 (s), 132.1 (s), 132.0 (s),128.6 (s), 127.7 (s), 127.5 (s), 126.8 (s), 126.5 (s)	76.4 (d, J = 25.5 Hz, MnC), 0.6 (s, SiC)	7.37
 $\underset{(C_6H_5)_2PH}{(CO)_4Mn}-\overset{O}{\overset{\parallel}{C}}-CH_2Si(CH_3)_3$ **6b**	7.75–7.68 (m, 4 H), 7.51–7.44 (m, 6 H), 6.44 (d, J_{HP} = 384 Hz, 1 H), 2.98 (s, 2 H), 0.14 (s, 9 H)	269.1 (d, J = 14.0 Hz, C=O), 218.8 (d, J = 7.0 Hz, C≡O), 215.6, 215.4, 215.3 (2C≡O + 1C≡O, ^{31}P couplings unassigned)	*o*, 132.6 (d, J = 8.8 Hz); *i*, 132.2 (d, J = 43.8 Hz); *p*, 131.1 (s); *m*, 129.5 (d, J = 9.8 Hz)	60.0 (s, CH_2), −0.95 (s, SiC)	47.1
 $\underset{(C_6H_5)_2PSi(CH_3)_3}{(CO)_4Mn}-H$ **8**	7.66–7.59 (m, 4 H), 7.48–7.43 (m, 6 H), 0.38 (d, J_{HP} = 5.9 Hz, 9 H), −7.39 (d, J_{HP} = 33.7 Hz, 1 H)	219.8 (s), 218.4 (d, J = 18.0 Hz, 2C≡O), 217.4 (d, J = 14.0 Hz)	*i*, 134.2 (d, J = 30.0 Hz); *o*, 133.6 (d, J = 9.1 Hz); *p*, 129.9 (s); *m*, 129.0 (d, J = 9.1 Hz)	−1.89 (d, J = 9.0 Hz, SiC)	2.46
 $\underset{(C_6H_5)_2PH}{(CO)_4Mn}-H$ **9**	7.78–7.70 (m, 4 H), 7.57–7.47 (m, 6 H), 6.70 (dd, J_{HP} = 356 Hz, J_{HH} = 3.1 Hz, 1 H), −7.44 (dd, J_{HP} = 41.6 Hz, J_{HH} = 3.1 Hz, 1 H)	218.9 (s), 217.0 (d, J = 23.0 Hz, 2C≡O), 216.7 (d, J = 17.9 Hz)	*o*, 132.7 (d, J = 12.3 Hz); *i*, 132.5 (d, J = 45.8 Hz); *p*, 131.1 (s); *m*, 129.4 (d, J = 8.2 Hz)		40.0 (d, J_{HP} = 355 Hz)[g]

[a] At 300 MHz in CD_2Cl_2, ambient probe temperatue, and referenced to CD_2Cl_2 (δ 5.32) unless noted. [b] At 75 MHz in CD_2Cl_2, −20 °C, and referenced to CD_2Cl_2 (53.8 ppm) unless noted. [c] All couplings are to phosphorus. [d] Ipso carbon designated by *i*. [e] At 121 MHz in CD_2Cl_2, ambient probe temperature, and referenced to external H_3PO_4 unless noted. [f] In CO_3CN and referenced to $(CH_3)_4Si$. [g] From a coupled spectrum.

5-mm NMR tube was charged with $(CO)_5MnCH_3$ (**2a**, 0.0982 g, 0.468 mmol), **3** (0.111 g, 0.430 mmol), and CH_2Cl_2 (0.5 mL) and was capped with a septum and shaken. The reaction was monitored by ^{1}H NMR. Between 12 and 13 h were required for the methyl resonance of **3** to disappear. Hexanes were then added to the tube, and the solution was filtered through a 15-mL fritted (M) funnel containing a plug of flame-dried silica gel. The plug was washed with ca. 100 mL of hexanes. Solvent was removed

Table II. Key IR and Mass Spectral Data for New Organometallic Compounds

compd	IR,[a] cm^{-1}	mass spectrum, *m/e* (relative intensity)
2a	$\nu_{C\equiv O}$ 2054 ms, 1980 s, 1962 vs, 1943 vs	468 (M$^+$, 5), 440 (M$^+$ − CO, 3), 356 (M$^+$ − 4CO, 100), 144 (20)[b,c]
2b	$\nu_{C\equiv O}$ 2053 m, 2048 ms, 1978 m, 1974 ms, 1962 s, 1956 s, 1941 vs	540 (M$^+$, 1), 428 (M$^+$ − 4CO, 10), 144 (2), 73 ($^+$Si(CH$_3$)$_3$, 100)[b,c]
2c	$\nu_{C\equiv O}$ 2057 ms, 1983 s, 1966 vs, 1945 vs	530 (M$^+$, 14), 502 (M$^+$ − CO, 28), 474 (M$^+$ − 2CO, 17), 418 (M$^+$ − 4CO, 100), 144 (1)[b,c]
2d	$\nu_{C\equiv O}$ 2057 ms, 1983 s, 1967 vs, 1945 vs	522 (M$^+$ − CO, 5), 468 (M$^+$ − 4CO, 100), 144 (7)[b,c]
6b	$\nu_{C\equiv O}$ 2061 m, 1984 s sh, 1974 vs, 1955 s; $\nu_{C=O}$ 1611 m br	
8	$\nu_{C\equiv O}$ 2059 m, 1982 ms, 1963 vs, 1956 s	426 (M$^+$, 1), 314 (M$^+$ − 4CO, 58), 259 ((C$_6$H$_5$)$_2$PHSi(CH$_3$)$_3$$^+$, 100)[d]
9	ν_{P-H} 2327 vw br; $\nu_{C\equiv O}$ 2068 ms, 1992 s, 1979 vs, 1964 s	

[a] In hexanes. [b] At 15 eV. [c] At 70 eV, peaks at *m/e* 144 and 73 ($^+$Si(CH$_3$)$_3$) intensify. [d] At 70 eV.

from the filtrate by rotary evaporation, and the residue was vacuum dried to give **3a** (0.151 g, 0.322 mmol, 75%) as a yellow oil. The oil was taken up in petroleum ether, and the resulting solution was concentrated to <1 mL and stored overnight at −40 °C. Lemon yellow crystals of **4a** formed which were collected on a cold frit (most of **4a** remained in solution), washed with cold petroleum ether, and vacuum dried: mp 55–59 °C (capillary sealed under N$_2$). Anal. Calcd for $C_{21}H_{22}MnO_5PSi$: C, 53.85; H, 4.73. Found: C, 53.59; H, 4.85.

Synthesis of $(CO)_4\overline{MnC(CH_2Si(CH_3)_3)(OSi(CH_3)_3)P}(C_6H_5)_2$ (4b). A 5-mm NMR tube was charged with **2b** (0.116 g, 0.411 mmol), **3** (0.100 g, 0.387 mmol), and benzene (0.5 mL) and was capped with a septum and shaken. After 2.5 h, hexanes was added to the tube. This mixture was filtered through a Pasteur pipet containing flame-dried Florisil. The Florisil was washed with additional hexanes. Solvent was removed from the filtrate by rotary evaporation. Crude crystals of **4b** formed, which were dissolved in petroleum ether. This solution was concentrated by using a N$_2$ stream until crystals were observed. This mixture was stored overnight at −40 °C. Yellow crystals of **4b** were collected on a cold frit, washed with cold petroleum ether, and vacuum dried (0.110 g, 0.203 mmol, 52%); decomp pt 118.5–120.5 °C (capillary sealed under N$_2$).

Synthesis of $(CO)_4\overline{MnC(C_6H_5)(OSi(CH_3)_3)P}(C_6H_5)_2$ (4c). A. A Schlenk flask was charged with $(CO)_5MnC_6H_5$ (**2c**, 0.152 g, 0.559 mmol), **3** (0.155 g, 0.600 mmol), and benzene (15 mL) and was fitted with a condenser. The reaction was refluxed for 2 h and was then allowed to cool. An equal volume of hexanes was added. This mixture was filtered through a 15-mL fritted (M) funnel containing a plug of flame-dried Florisil. The Florisil was washed with additional hexanes (ca. 150 mL). Solvent was removed from the filtrate by rotary evaporation, and the resulting oily residue was taken up in a minimum amount of petroleum ether (35–60 °C). This solution was concentrated to <1 mL and stored overnight, during which time crystals appeared. This mixture was then stored at −40 °C for 2–3 h. Lemon yellow crystals of **4c** were collected on a cold frit, washed with cold petroleum ether, and vacuum dried (0.200 g, 0.377 mmol, 67%): decomp pt 107.5–108.5 °C (capillary sealed under N$_2$). Anal. Calcd for $C_{26}H_{24}MnO_5PSi$: C, 58.86; H, 4.57; Mn, 10.36; P, 5.84; Si, 5.29. Found: C, 58.69; H, 4.49; Mn, 10.51; P, 6.01; Si, 5.07. **B.** A Schlenk tube was charged with $(CO)_5MnCOC_6H_5$ (0.082 g, 0.27 mmol), **3** (0.075 g, 0.29 mmol), benzene (6 mL), and a stir bar. The reaction was stirred at 40 °C for 14 h. Product **4c** (0.088 g, 0.17 mmol, 63%) was isolated as described in A and identified by its IR spectrum.

Synthesis of $(CO)_4\overline{MnC(2\text{-}C_{10}H_7)(OSi(CH_3)_3)P}(C_6H_5)_2$ (4d). A Schlenk flask was charged with **2d** (0.152 g, 0.472 mmol), **3** (0.130 g, 0.503 mmol), and benzene (15 mL) and was fitted with a condenser. The reaction was refluxed for 2.5 h and was then allowed to cool. Solvent was then removed under oil pump vacuum. The residue was chromatographed in air on a 3 × 37 cm flame-dried Florisil column using 98:2 (v/v) hexanes/ethyl acetate. The product fraction was collected under a N$_2$ purge, and the remainder of the workup was conducted under N$_2$. Solvent was removed from the product fraction by rotary evaporation. The resulting oily residue was crystallized as described for **4c** except the −40 °C cooling step was omitted. Lemon yellow crystals of **4d** (0.144 g, 0.196 mmol, 42%) were obtained: decomp pt 127–129 °C (capillary sealed under N$_2$). Anal. Calcd for $C_{30}H_{26}MnO_5PSi$: C, 62.07; H, 4.51; Mn, 9.46; P, 5.34; Si, 4.84. Found: C, 62.10; H, 4.61; Mn, 9.52; P, 5.42; Si, 4.95.

Synthesis of *cis*-$(CO)_4Mn(COCH_2Si(CH_3)_3)P(C_6H_5)_2H$ (6b). A. Complex **4b** (0.0836 g, 0.155 mmol) was chromatographed on a 2 × 32 cm silica gel column in 95:5 (v/v) hexanes/ethyl acetate. Two faint yellow bands were observed. The second was the product fraction, which was collected under a N$_2$ purge. The remainder of the workup was conducted under N$_2$. Solvent was removed from the product fraction by rotary evaporation. This gave **6** (0.063 g, 0.13 mmol, 84%) as a light yellow oil. The oil was dissolved in a minimum amount of petroleum ether (bp 35–60 °C) and cooled to −40 °C. Light yellow crystals of **6b** formed and were collected by filtration: decomp pt 74–78.5 °C (capillary sealed under N$_2$). Anal. Calcd for $C_{21}H_{22}MnO_5PSi$: C, 53.85; H, 4.73; Mn, 11.73; P, 6.61; Si, 6.00. Found: C, 54.12; H, 4.90; Mn, 11.60; P, 6.74; Si, 5.88. **B.** A 5-mm NMR tube was charged with **2b** (0.088 g, 0.31 mmol), $(C_6H_5)_2PH$ (0.055 g, 0.30 mmol), and benzene (0.5 mL) and was capped with a septum and shaken. The reaction was monitored by ^{1}H NMR and was complete after 3 h. Hexanes was added to the tube and this solution was chromatographed as in A. Product **6b** was obtained as a light yellow oil (0.128 g, 0.273 mmol, 91%).

Synthesis of *cis*-$(CO)_4Mn(H)P(C_6H_5)_2Si(CH_3)_3$ (8). A round-bottom flask was charged with a solution of $(CO)_5MnH$ (0.145 g, 0.740 mmol) in hexanes (1 mL) and a stir bar. The solution was stirred, and **3** (0.180 g, 0.697 mmol) in hexanes (1 mL) was added. Additional hexanes (1 mL) were added. After 2.5 h, solvent was removed by rotary evaporation. More hexanes were added, and the rotary evaporation was continued to remove the last traces of $(CO)_5MnH$. The residue was taken up in hexanes and filtered through a Pasteur pipet containing flame-dried Florisil. The Florisil was rinsed with additional hexanes (ca. 25 mL). Solvent was removed from the filtrate by rotary evaporation. The resulting crystals of **8** were dissolved in petroleum ether (bp 35–60 °C). This solution was concentrated to ca. 1 mL and was stored overnight at −40 °C. Very air-sensitive, light yellow crystals of **8** formed and were collected on a cold frit, washed with cold petroleum ether, and vacuum dried (0.227 g, 0.532 mmol, 76%): mp 102–104 °C (capillary sealed under N$_2$).

Synthesis of *cis*-$(CO)_4Mn(H)P(C_6H_5)_2H$ (9). This compound was prepared from $(CO)_5MnH$ (0.148 g, 0.755 mmol) and $(C_6H_5)_2PH$ (0.131 g, 0.704 mmol) by a procedure similar to that used for **8**. The reaction time was 3 h. Complex **9** (0.229 g, 0.599 mmol, 85%) was obtained as a very air-sensitive light yellow liquid following rotary evaporation and drying (1 h, 25 °C) under vacuum.

Rates of Reactions of $(CO)_5MnC_6H_5$ (2c) and $(CO)_5MnCOC_6H_5$ with 3. A 5-mm NMR tube was charged with **2c** (0.014 g, 0.051 mmol), **3** (0.012 g, 0.046 mmol), and C_6H_6 (0.52 mL). The tube (0.098 M in **2c**; 0.088 M in **3**) was capped with a septum, shaken, and placed in a 40 °C oil bath. The reaction was periodically monitored by ^{1}H NMR. The disappearance of the Si(CH$_3$)$_3$ resonance of **3** took ca. 40 h.

A 5-mm NMR tube was charged with $(CO)_5MnCOC_6H_5$ (0.063 g, 0.21 mmol), **3** (0.049 g, 0.19 mmol), and C_6H_6 (2.1 mL). The tube (0.10 M in $(CO)_5MnCOC_6H_5$; 0.090 M in **3**) was capped with a septum, shaken, and placed in a 40 °C oil bath. The disappearance of the $Si(CH_3)_3$ resonance of **3** required 13–14 h.

Rate of Reactions of $(CO)_5MnCH_3$ (2a) with 3 and $(C_6H_5)_3P$. A 5-mm NMR tube was charged with **2a** (0.040 g, 0.19 mmol), **3** (0.054 g, 0.21 mmol), and CH_2Cl_2 (0.35 mL). The tube (0.54 M in **2a**; 0.60 M in **3**) was capped with a septum, shaken, and left at 21 °C. The reaction was periodically monitored by ^1H NMR. The half-life of **2a** was ca. 2.2 h, as assayed by the disappearance of the $MnCH_3$ resonance.

A 5-mm NMR tube was charged with **2a** (0.039 g, 0.19 mmol), $(C_6H_5)_3P$ (0.054 g, 0.21 mmol), standard $(C_6H_5)_3SiCH_3$ (0.053 g, 0.19 mmol), and CH_2Cl_2 (0.35 mL). The tube (0.54 M in **2a**; 0.60 M in $(C_6H_5)_3P$) was capped with a septum and monitored as above. The half-life of **2a** was ca. 2.5 h.

A 5-mm NMR tube was charged with **2a** (0.022 g, 0.10 mmol) and 0.36 mL of a CH_2Cl_2 solution which was 0.96 M in $(C_6H_5)_3P$ (0.35 mmol), 0.96 M in **3** (0.35 mmol), and 0.046 M in $Cr(acac)_3$ (0.017 mmol). The reaction was monitored by ^{31}P NMR at ambient probe temperature by using a pulse delay of 20 s. Integration of the resonances due to $(C_6H_5)_3P$ and **3** in the starting solution (without **2a**) and after 20-, 40-, and 60-min reaction times indicated that **3** was consumed ca. 1.1 times faster than $(C_6H_5)_3P$.

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Registry No. **2a**, 13601-24-6; **2b**, 29992-26-5; **2c**, 13985-77-8; **2d**, 88916-68-1; **3**, 17154-34-6; **4a**, 88932-93-8; **4b**, 88916-69-2; **4c**, 88916-70-5; **4d**, 88916-71-6; **6b**, 88916-72-7; **8**, 88916-73-8; **9**, 100790-19-0; C_6H_5COCl, 98-88-4; $K^+(CO)_5Mn^-$, 15693-51-3; $(C_6H_5)_2PCl$, 1079-66-9; $(CH_3)_3SiCl$, 75-77-4; $(CH_3)_3SiCH_2Li$, 1822-00-0; $(CH_3)_3SiCH_2Cl$, 2344-80-1; $(CO)_5MnBr$, 14516-54-2; $(CO)_5MnCOC_6H_5$, 15612-92-7; $(CO)_5MnH$, 16972-33-1; $(C_6H_5)_2PH$, 829-85-6; $(C_6H_5)_3P$, 603-35-0; 2-naphthoyl chloride, 2243-83-6.

Electrochemical Synthesis and Properties of $(\eta^5\text{-}C_5H_4R)_2TiSe_5$ (R = H, Me, *i*-Pr)

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Ultrasound-induced electrochemical reduction of gray Se powder in DMF or THF, followed by addition of $(\eta^5\text{-}C_5H_4R)_2TiCl_2$ (**1**, R = H, *i*-Pr), led to $(\eta^5\text{-}C_5H_4R)_2TiSe_5$ (**2**, R = H, *i*-Pr) in high current efficiencies in THF and low to moderate yields in DMF. Compounds **2** could be also prepared in moderate yields when **1** was reduced at a Pt cathode in THF, in the presence of an excess of Se (at least 5 equiv). Finally, **2** was obtained in low yields when **1** was chemically reduced to the dimeric form $(\eta^5\text{-}C_5H_4R)_2TiCl$ (**3**), gray Se powder being added after reduction. From the electrochemical results, it is suggested that a key step of the overall process leading to **2** is a one-electron reduction of complex **1**, followed by formation of complex **3**. In the first electrochemical method, an homogeneous electron transfer would occur between an electrochemically generated Se anionic species and complex **1**. The lower yields of **2** in DMF than in THF are in agreement with the better binding properties of DMF, compared to THF, as far as complex **3** is concerned. Complexes **2** were irreversibly reduced and worked as a soluble Se reservoir. The electrochemical synthesis of **2** (R = Me) was thus achieved in 70% yield.

Introduction

The pentaselenide complexes **2** (R = H, CH_3) are suitable substrates for Se atom transfer.[1-4] They are readily available materials from chemically prepared alkali polyselenides and the titanocene dichlorides **1** (R = H, CH_3) according to the overall reaction (1).[4-7]

$$\underset{\mathbf{1}}{(\eta^5\text{-}C_5H_4R)_2TiCl_2} + (M_2^{2+}, Se_5^{2-}) \rightarrow \underset{\mathbf{2}}{(\eta^5\text{-}C_5H_4R)_2TiSe_5} + 2MCl \quad (1)$$

Very recently,[8] we have observed that the ultrasound-induced electrochemical reduction of Se powder proceeds very easily in solvents such as *N*,*N*-dimethylformamide (DMF), CH_3CN, and tetrahydrofuran (THF) in which gray selenium is insoluble. Addition of an alkyl halide, RX, to the electrogenerated anions Se_2^{2-} and Se^{2-} leads to the corresponding dialkyl diselenide RSeSeR and dialkyl selenide RSeR in a double nucleophilic substitution reaction. However, in certain cases, the indirect reduction of RX by Se_2^{2-} or Se^{2-} occurs simultaneously.[9]

In the present report, we describe the electrochemical synthesis in DMF and THF of the pentaselenide complexes **2a,b** from electrochemically generated polyselenide anions and titanocene dichlorides **1a,b**. A second electrochemical method and its chemical equivalent are successfully proposed to perform the syntheses of complexes **2a,b**. The influence of the solvent on their yields is discussed. The electrochemical behavior of complexes **2a,b** is examined, and it is shown that these pentaselenide derivatives can serve as a soluble Se reservoir.

$(\eta^5\text{-}C_5H_4R)_2TiCl_2$	$(\eta^5\text{-}C_5H_4R)_2TiSe_5$
1a, R = H	**2a**, R = H
1b, R = *i*-Pr	**2b**, R = *i*-Pr
1c, R = *t*-Bu	**2c**, R = *t*-Bu
1d, R = CH_3	**2d**, R = CH_3

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