for 20 h at 50 °C; afterward, it was cooled to room temperature and evaporated under reduced pressure. The residue was extracted with 5 mL of benzene, and the solution was eluted on a column of Grade III Woelm alumina (2 × 40 cm) with benzene. The eluate was collected in 50-mL portions; all portions showing a CN stretch in the IR spectrum were combined. Evaporation to a white powder and crystallization from CH_2Cl_2 with hexane at −20 °C gave colorless crystals of $CpW(CO)_2(CNMe)SnPh_3$ (0.14 g, 63%). Anal. Calcd for $C_{27}H_{23}NO_2SnW$: C, 46.59; H, 3.34. Found: C, 46.74; H, 3.50.

Repeating this procedure with *cis*-$CpW(CO)_2(CS)PbPh_3$ (0.27 g, 0.34 mmol) gave yellow needles of $CpW(CO)_2(CNMe)PbPh_3$ (0.08 g, 30%). Anal. Calcd for $C_{27}H_{23}NO_2PbW$: C, 41.33; H, 2.96. Found: C, 41.50; H, 3.04.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Grant No. CHE75-15147).

Registry No. CpW(CO)(CS)NO, 77827-50-0; $HB(pz)_3W(CO)(CS)NO$, 77846-73-2; $CpW(CO)_2CS$–DNP, 77827-51-1; $CpW(CO)(PPh_3)CS$–Ph, 72303-52-7; $HB(pz)_3W(CO)_2CS$–Me, 77827-54-4; $HB(pz)_3W(CO)_2CS$–Et, 77846-72-1; $HB(pz)_3W(CO)_2CS$–DNP, 77827-55-5; CpW(CO)(CNMe)NO, 77827-52-2; $HB(pz)_3W(CO)(CNMe)NO$, 77827-53-3; *cis*-$CpW(CO)_2(CNMe)SnPh_3$, 77881-61-9; *trans*-$CpW(CO)_2(CNMe)SnPh_3$, 77827-56-6; *cis*-$CpW(CO)_2(CNMe)PbPh_3$, 77827-57-7; *trans*-$CpW(CO)_2(CNMe)PbPh_3$, 77880-85-4; $Bu_4N[CpW(CO)_2CS]$, 74989-73-4; $Bu_4N[HB(pz)_3W(CO)_2CS]$, 75008-92-3; $CpW(CO)(PPh_3)(CS)I$, 72303-51-6; *trans*-$HB(pz)_3W(CO)_2(CS)I$, 77827-58-8; *cis*-$CpW(CO)_2(CS)SnPh_3$, 77880-86-5; *cis*-$CpW(CO)_2(CS)PbPh_3$, 74989-75-6; *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, 80-11-5; $NOPF_6$, 16921-91-8; DNP–Cl, 97-00-7; MeI, 74-88-4; EtI, 75-03-6; PhLi, 591-51-5; MeLi, 917-54-4; $MeNH_2$, 74-89-5.

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720,
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Reactions of (η^5-Cyclopentadienyl)cobalt(III) Alkyls with Cobalt(I) Phosphines and Iron Carbonyls. Evidence for Direct η^5-Cyclopentadienyl and Trimethylphosphine Group Transfer between Metal Centers

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Received January 23, 1981

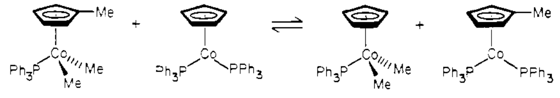
We have found that (η^5-methylcyclopentadienyl)(triphenylphosphine)dimethylcobalt(III) (**1**) undergoes intermolecular cyclopentadienyl ligand exchange with (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt(I) (**2**). The unsubstituted cyclopentadienyl(triphenylphosphine)dimethylcobalt(III) (**3**) reacts in two different types of processes, with both $Fe_2(CO)_9$ and $Fe(CO)_5$. The first involves electrophilic displacement of coordinated phosphine by unsaturated $Fe(CO)_4$, and the second takes place by abstraction of CO from $Fe(CO)_5$ by the unsaturated $CpCoMe_2$ fragment (generated by phosphine dissociation from the saturated starting material).

Introduction

Alkyl groups are easily transferred between many types of metal centers, apparently by a number of different mechanisms. The best understood of these processes are those in which a metal alkyl interacts with a second metal in a higher oxidation state and are usually thought of as involving electrophilic attack of the high-oxidation-state center upon the metal–carbon bond.[1]

A number of formally symmetrical alkyl-transfer reactions have also been uncovered recently. In the majority of these, alkyl transfer is assisted by transfer of halogen or another electronegative group in the opposite direction,[2] but cooperative transfer of two alkyl groups (as well as examples of stable dialkyls in which the alkyl groups bridge two metal centers) is now known.[3,4]

Transfer of an alkyl group from a metal center to a second center in a *lower* oxidation state (i.e., attack at metal-bound carbon by a second, nucleophilic, metal center) is less common.[5] During a recent study of pairwise exchange of methyl groups between the Co(III) centers in $CpCoLR_2$ complexes,[4] we considered the possibility that traces of a cobalt(I) complex, $CpCo(PPh_3)_2$, might contribute to the alkyl-transfer reactivity of the system. We have now examined that possibility directly and have found reactions such as that shown in eq 1 occur with relative ease. However, the mechanism surprisingly involves *cyclopentadienyl* rather than alkyl transfer. We report here the details of this study, as well as some observations on reactions of cobalt(III) dimethyl complexes with several other low-valent metal complexes.



(1)

1 2 3 4

Results and Discussion

Reaction of $MeCpCo(PPh_3)Me_2$ (1) with $CpCo(PPh_3)_2$ (2). When a solution of **1** and $CpCo(PPh_3)_2$ (**2**) in THF-d_8 was heated in a sealed NMR tube at 62 °C, new methyl resonances arising from the unsubstituted methyl analogue **3** were observed in the ^1H NMR spectrum; AA′BB′ Cp resonances corresponding to $MeCpCo(PPh_3)_2$ (**4**) were also seen (cf. eq 1). After 48 h the reaction had apparently reached equilibrium, with NMR observations showing a 67:33 ratio of **1** and **3**. The cobalt(III) complexes could be removed from this mixture by chromatography under air-free conditions and recrystallized together from benzene/hexane solvent. Because

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* To whom correspondence should be addressed at the University of California.

(1) See, for example: (a) Leslie, J. P.; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4839. (b) Johnson, M. D. *Acc. Chem. Res.* **1978**, *11*, 57 and references cited there. (c) Jawad, J. K.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1977**, 892.

(2) (a) Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1811. (b) Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1219. (c) Thompson, P. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1975**, 841.

(3) (a) Jolly, P. W.; Jonas, K.; Kruger, C.; Tsay, Y.-H. *J. Organomet. Chem.* **1970**, *33*, 109. (b) Kruger, C.; Sekutowski, J. C.; Berke, H.; Hoffman, R. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1110. (c) Holton, J. H.; Lappert, M. F.; Ballard, D. G. H.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45, 54.

(4) Bryndza, H. E.; Bergman, R. G.; Evitt, E. R. *J. Am. Chem. Soc.* **1980**, *102*, 4948.

(5) (a) Dodd, D.; Johnson, M. D. *J. Chem. Soc., Chem. Commun.* **1971**, 1371. (b) Dodd, D.; Johnson, M. D.; Lockman, B. L. *J. Am. Chem. Soc.* **1977**, *99*, 3664. (c) Magnuson, R. H.; Halpern, J. H.; Levitin, I. Ya.; Vol'pin, M. E. *J. Chem. Soc., Chem. Commun.* **1978**, 44.

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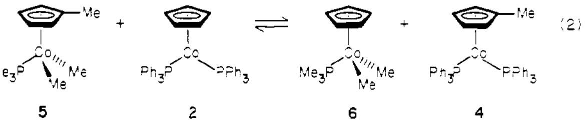
Table I. Rates of Phosphine Substitution of $CpCo(PPh_3)Me_2$ with PMe_3 [a]

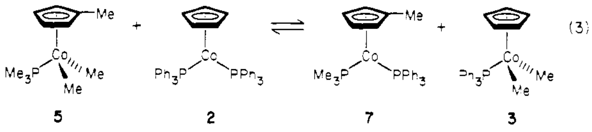
expt	T, K	k_d, s^{-1}
1	288.15	3.96×10^{-5}
2	303.15	4.38×10^{-4}
3	303.15	4.49×10^{-4}
4	318.15	4.85×10^{-3}

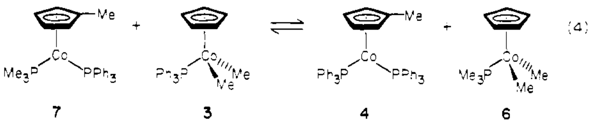
[a] Experiments run with 10 equiv of PMe_3 in a toluene solution of dimethyl complex 3. [b] Standard deviation ±1%.

1 and **3** could not be separated in this way, each pure complex was prepared independently, and synthetic mixtures were shown to be identical with the material isolated from the exchange reaction. Reaction of **1** and **2** in the presence of about 10 equiv of PPh_3-d_{15} (deuterated phosphine was used to facilitate acquisition of FT ^1H NMR data) was only slightly slower (a factor of 2) than the reaction run in the absence of added phosphine.

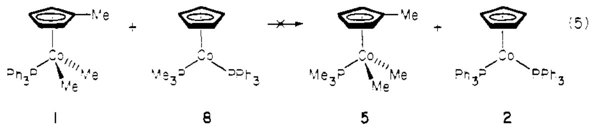
Reaction of $MeCpCo(PMe_3)Me_2$ (5) with $CpCo(PPh_3)_2$ (2). Reaction 1 might take place by either one of two pathways: phosphine and methyl ligand exchange or cyclopentadienyl ring exchange. Previous studies have shown that phosphine substitution lability in these complexes is highly dependent upon both cobalt oxidation state and the nature of the phosphine involved.[6] For example, **2** undergoes dissociation of PPh_3 rapidly even at −60 °C;[6a] in the presence of PMe_3 this gives the less reactive $CpCo(PPh_3)(PMe_3)$, and ultimately the still less reactive $CpCo(PMe_3)_2$ is formed. Previous experiments[6b,c] have demonstrated that phosphine substitution of complex **3** takes place through dissociation of PPh_3 and subsequent trapping of the unsaturated $CpCoMe_2$ intermediate so generated. Rates of that dissociation step were measured at various temperatures, as seen in Table I. Activation parameters have been derived from a plot of ln k vs. $1/T$ as $E_a = 29.2 \pm 0.7$ kcal/mol, $\Delta H^{\ddagger} = 28.6 \pm 0.6$ kcal/mol, $\Delta S^{\ddagger} = 20.3 \pm 0.6$ eu (at 300 K). These parameters predict a rate of dissociation of PPh_3 of 3.81×10^{-2} s^{-1} at 60 °C. However the corresponding PMe_3 complex **6** is quite inert to substitution under these conditions. Thus it is possible to in effect "label" the cobalt(III) atom in a $MeCpCo(L)Me_2$ complex with the tightly bound PMe_3 ligand. Accordingly, complex **5** was heated in THF-d_8 with the cobalt(I) PPh_3 complex **2**. Surprisingly, this reaction (eq 2) proceeded at a rate similar to that of reaction 1 at 62 °C, and the products were found to be **6** and **4** (at equilibrium, the ratio of **5** to **6** is ca. 60:40), again by comparison with independently prepared samples. Simple methyl exchange would be expected to have given **3** and the mixed-phosphine complex $MeCpCo(PMe_3)(PPh_3)$ (**7**). The observed products suggest that cyclopentadienyl ligand exchange has taken place.







Reaction of 1 with $CpCo(PPh_3)(PMe_3)$ (8). One possible way reaction 2 might be occurring without Cp ligand transfer is illustrated in eq 3 and 4. Here it is postulated that phosphine/methyl transfer occurs to give transient amounts of **7** and **3**, and these complexes react rapidly (perhaps by PPh_3 dissociation from **3** and some sort of direct bimolecular PMe_3 transfer) to give **4** and **6**. In order to see whether such a direct reaction could occur, we heated the analogous complexes **1** and **8** (eq 5) under conditions where both reactions 1 and 2 took place. No reaction was observed, indicating that eq 4 does not take place. At higher temperatures (80 °C) slow thermal decomposition of **1** was observed, but no phosphine exchange was noted. On the basis of this information Cp exchange is strongly implicated as being responsible for reactivity in this Co(I)/Co(III) system.



Reaction of 3 with Low-Valent Complexes. Although methyl exchange in reaction 1 has been ruled out, the question of whether such an exchange is possible in cases where some thermodynamic driving force favors that type of process is still an interesting one. For a brief survey of this type of reaction, **3** was allowed to react with several unsaturated transition-metal complexes which can undergo two-electron oxidations.

When **3** was heated in solutions containing $(PPh_3)_3RhCl$, no changes in the ^1H NMR spectra were noted below 80 °C. Above that temperature slow decomposition of **3** was observed but no evidence for alkyl exchange was obtained in a variety of solvents (THF-d_8, CD_2Cl_2, C_6D_6) regardless of whether or not excess triphenylphosphine was added to the solutions. Similarly, no reaction between $(PPh_3)_3IrCl$ and **3** was noted under a variety of conditions. In C_6D_6 and THF-d_8 $(PPh_3)_3IrCl$ was found to undergo unimolecular ortho metallation faster than reaction with **3**, at all temperatures between 25 and 100 °C. Finally, no methyl exchange between **3** and $(PPh_3)_2PtCl_2$ was observed in either THF-d_8 or CD_2Cl_2 with or without added phosphine.

In contrast to the above observations, cobalt alkyls *do* react with iron carbonyls. When **3** was allowed to react at 25 °C in THF-d_8 with excess $Fe_2(CO)_9$, high yields (>95% by NMR) of acetone and $CpCo(CO)_2$ were realized. Those compounds were identified by isolation and comparison with independently prepared samples. Infrared and NMR spectroscopy allowed us to tentatively identify the iron products as a mixture of $Fe(CO)_5$, $Fe_3(CO)_{12}$, and $(PPh_3)Fe(CO)_4$. This reaction took place in darkened solutions as well as in room light. Monitoring the reaction by ^1H NMR spectroscopy allowed detection of an unstable intermediate whose concentration built up to a small extent during the reaction (vide infra). Reaction of **3** with $Fe(CO)_5$ under the same conditions led to a similar product mixture, although the reaction was *faster* and more of the aforementioned intermediate was observed in the NMR spectrum. The intermediate was identified on the basis of its NMR (single resonances in THF-d_8 at 0.46 and 4.95 ppm in a ratio of 6:5) and IR (single CO absorbance at 2001 cm^{-1}) spectra as $CpCo(CO)Me_2$, which was previously detected[6b,c] during the carbonylation of $[CpCo(CO)(CH_3)]_2$ and **3**. This complex is known[6b,c] to rapidly produce acetone and $CpCo(CO)_2$ in the presence of CO and to decompose thermally to acetone at 25 °C.

$Fe(CO)_5$ only grudgingly exchanges PPh_3 for CO at elevated temperatures in the absence of any other catalysts. Yet clearly

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[6] (a) Janowicz, A. H.; Bryndza, H. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 1516. (b) Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 7003. (c) Evitt, E. R.; Bergman, R. G. *Ibid.* **1978**, *100*, 3237.

$Fe(CO)_5$ serves as a source of CO for (potentially) coordinatively unsaturated cobalt. A mechanism for this process (Scheme I) involving phosphine dissociation from **3** prior to reaction with $Fe(CO)_5$ explains the observed results. This mechanism involves the known dissociation of $Fe_2(CO)_9$ into $Fe(CO)_5$ and $Fe(CO)_4$ as an initiating step[7] (step a) and relies on the other previously studied steps b,[6] e,[8] and f[7] to explain the products obtained. The requirement of step b in this mechanism is supported by the absence of reaction between **6** and $Fe(CO)_5$ in THF-d_8; as pointed out earlier, **6** does not rapidly dissociate its phosphine ligand as **3** has been shown to do.

Scheme I

$$\text{(a) } Fe_2(CO)_9 \rightleftharpoons Fe(CO)_4 + Fe(CO)_5$$

$$\text{(b) } CpCoLMe_2 \rightleftharpoons CpCoMe_2 + L$$

$$\text{(c) } CpCoMe_2 + Fe(CO)_5 \rightarrow CpCo(CO)Me_2 + Fe(CO)_4$$

$$\text{(c}'\text{) } CpCoLMe_2 + Fe(CO)_4 \rightarrow CpCoMe_2 + LFe(CO)_4$$

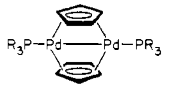
$$\text{(d) } CpCo(CO)Me_2 + 2Fe(CO)_5 \rightarrow CpCo(CO)_2 + 2Fe(CO)_4 + CH_3COCH_3$$

$$\text{(e) } Fe(CO)_4 + L \rightarrow LFe(CO)_4$$

$$\text{(f) } 3Fe(CO)_4 \rightarrow Fe_3(CO)_{12}$$

While Scheme I accounts for the acetone formed in the reaction between **3** and $Fe(CO)_5$, it suggests that no reaction should take place when **6** is combined in THF-d_8 with $Fe_2(CO)_9$. In fact, when that reaction was undertaken, a product mixture of acetone, $CpCo(CO)_2$, $(PMe_3)Fe(CO)_4$, $Fe(CO)_5$, and $Fe_3(CO)_{12}$ was obtained. To determine whether the $Fe(CO)_4$ produced from $Fe_2(CO)_9$ was responsible for the production of acetone in the reaction of **6** with $Fe_2(CO)_9$, we prepared the iron pyridine complex $(C_5H_5N)Fe(CO)_4$ and dissolved it in THF-d_8 containing complex **6**. The mixture was stable for a few hours at room temperature; heating the solution to 40 °C, where the $pyFe(CO)_4$ is known to dissociate CO,[9] resulted in the production of acetone, $CpCo(CO)_2$, and some $(PMe_3)(C_5H_5N)Fe(CO)_3$ as well as a complex mixture of higher iron clusters. Clearly, both $Fe(CO)_4$ and $Fe(CO)_5$ can react with these cobalt(III) complexes; the former can even remove bound phosphine from a cobalt(III) dialkyl, thus requiring a step such as c′ (Scheme I) to fully describe the reactivity of this system. We prefer to regard such a step c′ as electrophilic displacement of phosphine by unsaturated iron as the other obvious pathway (electron transfer) would result in instantaneous reductive elimination of ethane from the Co(IV) species so generated.[10] Stereochemical labeling experiments with optically active phosphines are needed to further establish the nature of this displacement.

Conclusions. Several surprising phenomena have been observed in this study. Exchange of cyclopentadienyl groups between transition-metal centers, albeit slowly in this case, appears to be quite rare;[11] certainly such transfer has not previously been observed between cobalt atoms in the general class of organometallic complexes discussed here. The nature of the transition state for this ligand transfer is unknown. However, the novel bridging-Cp complexes in the palladium series (e.g., A) recently discovered by Werner[12] provide an interesting model for such a transition state. It seems reasonable that in some complexes bridging systems have a free energy lower than their nonbridging analogues and are therefore isolable. In other systems, where mononuclear Cp complexes are more stable, Cp-bridging structures may be less stable but still energetically accessible, thus becoming possible transition states or intermediates for Cp-exchange processes.



A

Previously we observed that dissociation of a PPh_3 ligand from one metal center was required for exchange of methyl groups between cobalt centers; in light of this, the lack of inhibition of Cp exchange by excess PPh_3 was also unexpected. Since the overall Cp exchange process is slow and we know that ligand loss is relatively facile, this observation cannot be due to rate-determining PPh_3 dissociation followed by rapid exchange. Either the exchange occurs by interaction of two coordinatively saturated complexes or its rate is controlled by some process (e.g., $\eta^5 \rightleftharpoons \eta^3$ Cp rearrangement) other than phosphine ligand loss.

It is also clear from our results that $Fe(CO)_5$ can serve as a source of CO for unsaturated cobalt and that the unsaturated iron fragment $Fe(CO)_4$ has the ability to abstract PMe_3 from a (normally inert) Co(III) center.[13]

Experimental Section

General Data. All manipulations of oxygen- or water-sensitive materials were conducted under a prescrubbed recirculating atmosphere of N_2 in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train or with use of standard Schlenk or vacuum-line techniques.

Tetrahydrofuran (THF) and diethyl ether were distilled from purple sodium/benzophenone ketyl solutions. Benzene and hexanes were degassed and used as supplied from J. T. Baker ("Analyzed Reagent" grade). Methylene chloride (Baker "Analyzed Reagent" grade) was distilled from CaH_2 and degassed by freeze–pump–thaw cycles. Iron carbonyls ($Fe(CO)_5$ and $Fe_2(CO)_9$) were used as supplied from Alfa. $(PPh_3)_2PtCl_2$ (Alfa) was recrystallized from absolute ethanol, while $(PPh_3)_3RhCl$ (Alfa) was recrystallized from CH_2Cl_2/hexane. The $CpCo(PPh_3)Me_2$,[4,6c] $CpCo(PMe_3)Me_2$,[6c] $MeCpCo(PPh_3)Me_2$,[4] $MeCpCo(PMe_3)Me_2$,[4] $CpCo(PPh_3)_2$,[14] $CpCo(PPh_3)(PMe_3)$,[15] $Fe(CO)_4(PPh_3)$,[9] $Fe(CO)_4(NC_5H_5)$,[9] and $(PPh_3)_3IrCl$[16] were synthesized by previously published methods.

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 283 grating spectrophotometer using solutions of samples in sodium chloride cells (0.10-mm path length).

NMR Experiments. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM-390 90-MHz spectrometer or a high-field (180.09 MHz) instrument equipped with a Bruker magnet, Nicolet Technology Corp. Model 1180 data system, and electronics assembled by Mr. Rudi Nunlist (University of California at Berkeley). Spectra were recorded at probe temperatures (35 °C for the 90-MHz instrument and 25 °C for the high-field machine). Deuterated THF

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(8) (a) Cotton, F. A.; Parrish, R. V. *J. Chem. Soc.* **1960**, 1440. (b) Reickziefel, A.; Bigorgne, M. *J. Organomet. Chem.* **1965**, *3*, 341.

(9) (a) Schubert, E. H.; Sheline, R. K. *Inorg. Chem.* **1966**, *5*, 1071. (b) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 3438. (c) Flamini, A.; Semprini, E.; Stefani, F.; Cardaci, G.; Bellachioma, G.; Andreocci, M. *J. Chem. Soc., Dalton Trans.* **1978**, 695.

(10) White, M. A.; Mazenod, F. P.; Bergman, R. G., unpublished results.

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(13) Although we are not aware of other evidence for direct metal-assisted phosphine abstraction, evidence for metal-induced removal of CO has been reported. See, for example: Albers, M. O.; Coville, N. J., Ashworth, T. V.; Singleton, E.; Swanpoel, H. E. *J. Chem. Soc., Chem. Commun.* **1980**, 489. Our results do not provide information abut the detailed mechanism of this phosphine transfer; initial coordinative metal–metal bond formation could be involved as a first step in the process.

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(16) Bennett, M. A.; Milner, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 6983.

and benzene were vacuum transferred from sodium/benzophenone ketyl solutions while CD_2Cl_2 was vacuum transferred from Linde 4-Å molecular sieves and degassed through four freeze-pump-thaw cycles on a vacuum line.

NMR experiments were carried out as follows. A standard NMR tube fused to a 14/20 ground-glass joint was loaded with the desired compounds in the drybox, capped with a Teflon needle valve, placed on a vacuum line, and evacuated at -196 °C. The tube was charged with the desired amount of solvent by vacuum transfer out of a graduated tube of solvent. The NMR tube was sealed and carefully thawed before any heating cycles were undertaken. All heating was accomplished in a Precision Scientific model H-11 constant-temperature bath.

The phosphine inhibition experiment was set up by dissolving equal amounts of **1** (17.0 mg, 0.0397 mmol) and **2** (25.0 mg, 0.0386 mmol) into NMR tubes with joints. Into one tube was weighed 104 mg of PPh_3-d_{15} (0.376 mmol). The two tubes were then charged with toluene-d_8 solvent to bring the volume of the solutions to 600 μL. The tubes were sealed as before.

After completion of a reaction, the volatile components were vacuum transferred into another tube, under inert conditions, and analyzed by standard NMR, IR, VPC, and mass spectral methods. The nonvolatile components were then similarly isolated and analyzed by standard methods. Nonvolatile products of the iron reactions were analyzed as a mixture by NMR and IR comparisons to known compounds. Mixtures of cobalt alkyls were purified by air-free column chromatography on silica gel using benzene/hexane as the eluant. The mixture was recrystallized from benzene/hexane.

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Contribution from the Chemistry Department and Materials and Molecular Research Division of Lawrence Berkeley Laboratory,
University of California, Berkeley, California 94720

Preparation and Hydrogen-Deuterium Exchange of Alkyl and Hydride Bis(trimethylsilyl)amido Derivatives of the Actinide Elements

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The monomeric, hydrocarbon-soluble monohydrides and monodeuterides of the actinide metals (thorium or uranium) of the type $HM[N(SiMe_3)_2]_3$ have been prepared. Their reaction chemistry—*n*-BuLi followed by MeBr yields $MeM[N(SiMe_3)_2]_3$ and borane in tetrahydrofuran yields $BH_4M[N(SiMe_3)_2]_3$—suggests that the hydrogen atom is hydridic. Pyrolysis of the hydrides yields the novel, four-membered ring metallacycle $[(Me_3Si)_2N]_2\overline{MCH_2Si(Me)_2N}SiMe_3$ where M is Th or U. These metallacycles are the key intermediates in the hydrogen-deuterium exchange reaction that yields $\{[(CD_3)_3Si]_2N\}_3MD$.

Metal alkyl and hydride derivatives are important compounds in inorganic and organometallic chemistry.[1a] These functional groups are of interest in their own right as well as for their utility in organic synthesis.[1b,c] Though the organometallic and hydride derivatives of the p- and d-block elements are extensive, those of the f-block elements have been rather less extensively explored. The latter compounds are generally of the type Cp_3MR where M is an actinide element or Cp_2MR where M is a lanthanide element.[2] In contrast to the rather extensive alkyl chemistry, only two hydride derivatives, $(Me_5C_5)_4M_2H_4$ (M = Th or U), are known[3a,b] though attempts at their preparation have been described.[3c,d]

The large size and "hard" acid character of the actinide elements affords, as a natural consequence, compounds with high coordination numbers with nitrogen or oxygen ligands. For preparation of low-coordination-number, volatile, and hydrocarbon-soluble compounds of these metals, sterically bulky ligands are required. The bis(trimethylsilyl)amido ligand, $(Me_3Si)_2N$, is ideally suited for this task.[4] The steric bulk of this amide is shown, by way of example, by the observation that the uranium(III) species $[(Me_3Si)_2N]_3U$ is monomeric and three coordinate.[5] Further, the tetravalent methyl and tetrahydroborate derivatives $RM[N(SiMe_3)_2]_3$ where R is Me or BH_4 and M is Th or U are also monomeric.[6] Since the simple methyls and tetrahydroborates can be prepared readily there is no reason why the simple hydride species should not exist.[7]

Refluxing a tetrahydrofuran solution of 4 molar equiv of sodium bis(trimethylsilyl)amide and uranium or thorium tetrachloride yields the hydrides $HM[N(SiMe_3)_2]_3$, M = Th or U. The hydrides may also be prepared from $ClM[N(SiMe_3)_2]_3$ and 1 molar equiv of $NaN(SiMe_3)_2$ in refluxing tetrahydrofuran. Tetrahydrofuran is implicated as the hydrogen atom source since, if the latter reaction is conducted in refluxing diethyl ether, benzene, or isooctane, the starting chloro species $ClM[N(SiMe_3)_2]_3$ is recovered quantitatively. This inference is substantiated by using perdeuteriotetrahydrofuran as reaction solvent. In this solvent the deuteride $DM[N(SiMe_3)_2]_3$, M = Th or U, is isolated. The observation that tetrahydrofuran is the source of the hydrogen atom is not unique, as it has been observed previously.[8]

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