concerning orbital vs. charge control effects have appeared, but more research is needed before confident predictions can be made.

The manganese systems discussed in this paper are versatile not only for arene functionalization via Grignard reagents and ketone enolates but also may provide a useful route to polyfunctionalized cyclohexadienes.[7] Thus, the remarkably stable cyclohexadienyl complexes 2 can be "reactivated" by CO substitution with NO^+ to allow regioselective and stereoselective nucleophile addition to yield cyclohexadienes.

Acknowledgment. We are grateful to L. Grab for experimental assistance and valuable discussions. This work was supported by a grant from the National Science Foundation (No. CHE-8023964).

Registry No. 1 (arene = benzene), 38834-51-4; 1 (arene = chlorobenzene), 57812-91-6; 1 (arene = *p*-methylchlorobenzene), 57813-15-7; 1 (arene = toluene), 38834-27-4; 1 (arene = anisole), 57812-97-2; 2 (X = H, R = CH_2COCMe_3), 81857-37-6; 2 (X = H, R = CH_3), 59653-72-4; 2 (X = H, R = C_6H_5), 59592-95-9; 2 (X = 1-Cl, 4-CH_3; R = CH_3), 57812-88-0; 2 (X = 1-Cl, 4-CH_3; R = C_6H_5), 57812-87-0; 2 (X = 2-OCH_3, R = CH_3), 81857-38-7; 2 (X = 2-OCH_3, R = C_6H_5), 81857-39-8; 2 (X = 1-CH_3, 4-Cl; R = CH_3), 57872-11-4; 2 (X = 1-CH_3, 4-Cl; R = C_6H_5), 57872-09-0; $[(CH_3)(CN)_3Mn(CO)_3]PF_6$, 38833-22-6; biphenyl, 92-52-4; toluene, 108-88-3; *tert*-butyl benzyl ketone, 6721-67-1; pinacolone lithium enolate, 34865-75-3; CH_3Cl, 74-87-3; C_6H_5Br, 108-86-1.

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Substituent Effects upon Alkyl Migration to Coordinated CO. Syntheses and Carbonylation Studies of $(CO)_5MnCH_2I$ and $(CO)_5MnCH_2OSi(CH_3)_3$

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Iodide $ICH_2OSi(CH_3)_3$ is generated in situ from $H_2C{=}O$ and $(CH_3)_3SiI$ and then reacted with $K^+(CO)_5Mn^-$ to give α-(silyloxy)alkyl $(CO)_5MnCH_2OSi(CH_3)_3$ (1). Reaction of $(CO)_5MnSi(CH_3)_3$ (3) with $H_2C{=}O$ does not yield 1, and the addition of $(CH_3)_3SiI$ to $(CO)_5MnCH_2OCH_3$ gives instead iodomethyl complex $(CO)_5MnCH_2I$ (2) and $CH_3OSi(CH_3)_3$. While 1 is easily converted to acyl $(CO)_5MnCOCH_2OSi(CH_3)_3$ (7) under 200 psi of CO, 2 decomposes (to $(CO)_5MnI$ and/or $[(CO)_4MnI]_2$) faster than it carbonylates. The observed rates of carbonylation of 1 and reference alkyl $(CO)_5MnCH_2OCH_3$ are first order and independent of CO pressure over the 750–1500 psi range in acetonitrile. Average k_{obsd} at 24 °C are $(10.9 \pm 1.7) \times 10^{-4}$ s^{-1} and $(3.0 \pm 0.5) \times 10^{-4}$, respectively. Comparisons are made with the carbonylation rates of other $(CO)_5MnCH_2X$ compounds.

Introduction

Some time ago, we observed that the introduction of an α-$OSi(CH_3)_3$ substituent on alkyl $(CO)_5MnCH_2C_6H_5$ dramatically affected the rate of carbonylation.[2] While $(CO)_5MnCH_2C_6H_5$ showed no reaction after 1 h at 25 °C under 2000 psi of CO in THF, $(CO)_5MnCH(C_6H_5)OSi(CH_3)_3$ was 50% carbonylated to the corresponding acyl, $(CO)_5MnCOCH(C_6H_5)OSi(CH_3)_3$, under the same conditions (eq 1). Since α-oxy substituents normally *retard* the rate of metal alkyl carbonylation,[3] we have sought to determine if the parent molecule $(CO)_5MnCH_2OSi(CH_3)_3$ (1) shows similar anomalous reactivity. Carbonylation rate studies of $(CO)_5MnCH_2X$ compounds have been undertaken by several research groups,[3-7] so much useful comparative data are available.

In this paper, we describe the synthesis and carbonylation of $(CO)_5MnCH_2OSi(CH_3)_3$ (1). Despite its apparent simplicity, this molecule proved to be difficultly accessible. One attempted synthesis of 1 yielded $(CO)_5MnCH_2I$ (2), which is one of the few iodomethyl complexes known.[8,9] In view of recent interest in the use of iodide promoters in ruthenium-catalyzed $CO/H_2 \rightarrow$ glycol conversions,[10] we expanded our study to include attempts at the carbonylation of 2.

Results

Syntheses of 1 and 2. We previously reported that $(CO)_5MnSi(CH_3)_3$ (3) undergoes 1,2-addition to aldehydes (eq 2).[11] For instance, α-(silyloxy)alkyl $(CO)_5MnCH(C_6H_5)OSi(CH_3)_3$ (4, R = C_6H_5, eq 2) can be isolated from the reaction of benzaldehyde with 3. When adducts 4 contain a hydrogen β to the manganese, rapid decomposition to $(CO)_5MnH$ and a silyl enol ether takes place. However, in these cases 4 may be trapped as the corresponding acyl $(CO)_5MnCOCH(R)OSi(CH_3)_3$ by conducting eq 2 under CO.[11b,12]

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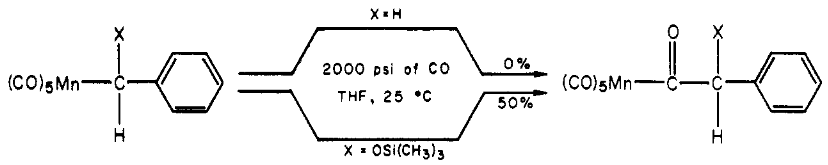

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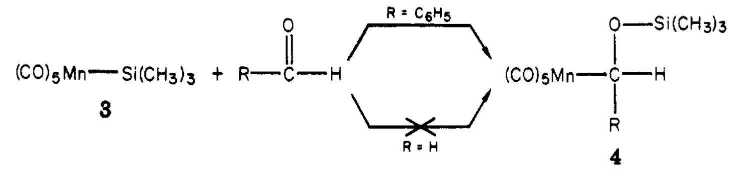

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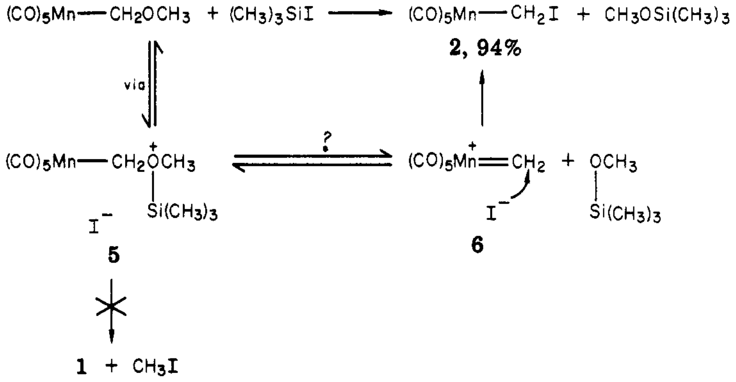

(3)

Table I. Spectroscopic Characterization of New Organometallic Compounds

compd	IR,[a] cm^{-1}	^1H NMR,[b] δ	^{13}C NMR,[c] ppm
$(CO)_5MnCH_2OSi(CH_3)_3$ 1	2116 (w) 2049 (w, sh) 2014 (s) 1999 (m, sh)	4.46 (s, 2 H) 0.09 (s, 9 H)	212.2 (cis C≡O) 209.5 (trans C≡O) 52.2 (CH_2) −1.9 ($SiCH_3$)
$(CO)_5MnCH_2I$ 2	2123 (w) 2063 (vw) 2049 (vw) 2029 (s) 2005 (m)	2.26 (s, 2 H)	210.7 (cis C≡O)[b,d] 207.9 (trans C≡O) −20.2 (CH_2)
$(CO)_5MnC(=O)CH_2OSi(CH_3)_3$ 7	2120 (w) 2052 (w, sh) 2023 (s) 2007 (m, sh) 1647 (w)	3.72 (s, 2 H) 0.15 (s, 9 H)	268.9 (acyl C=O) 209.0 (C≡O) 78.6 (CH_2) −1.8 ($SiCH_3$)

[a] In hexane. [b] In $CDCl_3$. [c] In CD_2Cl_2 at −53 °C unless noted. [d] −30 °C.

Accordingly, we attempted to synthesize $(CO)_5MnCH_2OSi(CH_3)_3$ (1) by treating formaldehyde (and its oligomers) with $(CO)_5MnSi(CH_3)_3$. Numerous reaction conditions were tried (polar and nonpolar solvents; use of *s*-trioxane, paraformaldehyde, and gaseous formaldehyde[13]), but no trace of 1 was detected. Similar reactions were conducted under CO, but no manganese acyl products were found. We concluded that under the conditions employed, monomeric formaldehyde underwent repolymerization faster than Mn–Si bond addition.

A second attempted synthesis of 1 utilized the Jung–Olah procedure[14,15] for the conversion of methyl ethers to $Si(CH_3)_3$ ethers. As shown in eq 3, $(CO)_5MnCH_2OCH_3$[2,16] was treated with 1.0 equiv of $(CH_3)_3SiI$. However, instead of 1, we obtained iodomethyl complex $(CO)_5MnCH_2I$ (2) as the exclusive organometallic product.

Complex 2 was characterized by spectral (Table I) and elemental analysis. However, in solution 2 underwent slow decomposition (CH_2Cl_2, several days; THF and ether, 10–12 h; CH_3CN, 2–4 h) to a mixture of $(CO)_5MnI$ and the red bridging diiodide $[(CO)_4MnI]_2$ (IR (hexane, cm^{-1}) 2093 (w), 2040 (s), 2015 (m), 1986 (s)).[17] Slow, purity-dependent, solid-state decomposition also occurred. The fate of the CH_2 group in 2 is presently under investigation.

The third route to 1 considered was the alkylation of $(CO)_5Mn^-$ by $XCH_2OSi(CH_3)_3$ electrophiles. Surprisingly, we were unable to find syntheses of $ClCH_2OSi(CH_3)_3$, $BrCH_2OSi(CH_3)_3$, or $ICH_2OSi(CH_3)_3$ in the literature.[18] This may in part be due to the fact that the conventional alcohol precursors to these silyl ethers, XCH_2OH, are not stable molecules. Since Jung had reported the 1,2 addition of $(CH_3)_3SiI$ to aldehydes to give labile $ICHROSi(CH_3)_3$ adducts,[19] we investigated the reaction of $(CH_3)_3SiI$ with monomeric formaldehyde. Gratifyingly, solutions were

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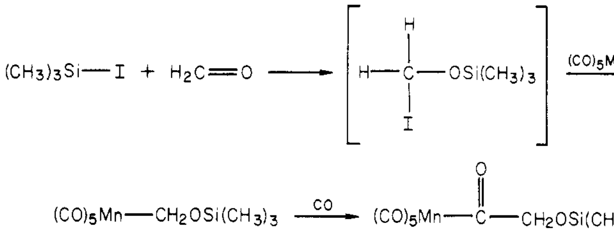
obtained which, upon reaction with $K^+(CO)_5Mn^-$, afforded good yields of **1** (eq 4). Although we could not isolate the presumed intermediate $ICH_2OSi(CH_3)_3$, the success of eq 4 constitutes good evidence for its formation. Solutions generated from *s*-trioxane and $(CH_3)_3SiI$ gave much lower yields of **1** upon treatment with $K^+(CO)_5Mn^-$.



(4)

1, 66% 7

Carbonylation Experiments. When **1** was treated with 200 psi of CO, facile carbonylation to $(CO)_5MnCOCH_2OSi(CH_3)_3$ (**7**; eq 4) occurred. Acyl **7** was characterized by spectral (Table I) and elemental analysis. However, when iodomethyl **2** was treated with 200–1500 psi of CO (both polar and nonpolar solvents; dilute and concentrated solutions), in no case could more than a trace of a possible acyl product be detected. The predominant product was always $(CO)_5MnI$; an 87% yield was obtained after **2** was treated with 1200 psi of CO for 18 h in CH_3CN.

The rate of carbonylation of **1** was measured at 750, 1000, and 1500 psi in CD_3CN at 24 °C (four to five data points/run). To provide a reference to a previously studied compound, we determined the rate of carbonylation of $(CO)_5MnCH_2OCH_3$ simultaneously in the same autoclave (but in a separate flask). In each case, the rate law $d[\text{alkyl}]/dt = -k_{obsd}[\text{alkyl}]$ was followed. Within experimental error, there was no dependence upon CO pressure. For **1**, k_{obsd} of $(10.6 \pm 1.7) \times 10^{-4}\ s^{-1}$ (750 psi), $(12.4 \pm 2.0) \times 10^{-4}\ s^{-1}$ (1000 psi), and $(9.6 \pm 1.5) \times 10^{-4}\ s^{-1}$ (1500 psi) were determined. For $(CO)_5MnCH_3OCH_3$, k_{obsd} of $(3.0 \pm 0.5) \times 10^{-4}\ s^{-1}$ (750 psi), $(3.1 \pm 0.5) \times 10^{-4}\ s^{-1}$ (1000 psi), and $(2.8 \pm 0.5) \times 10^{-4}\ s^{-1}$ (1500 psi) were determined. These data give average k_{obsd} of $(10.9 \pm 1.7) \times 10^{-4}\ s^{-1}$ (**1**) and $(3.0 \pm 0.5) \times 10^{-4}\ s^{-1}$ ($(CO)_5MnCH_2OCH_3$). Thus under the conditions investigated, an α-$OSi(CH_3)_3$ substituent provides a modest carbonylation rate enhancement over an α-OCH_3 substituent.

The rate of disappearance of **2** was monitored in CD_3CN under 750 psi of CO. Plots of $-\ln\{[\mathbf{2}]/[\mathbf{2}]_0\}$ vs. time deviated somewhat from linearity, but the data could be used to bound the k_{obsd} for a hypothetical carbonylation as $\leq 1.7 \times 10^{-4}\ s^{-1}$. In CH_2Cl_2 under 1300 psi of CO, the carbonylation k_{obsd} was bounded as $\leq 0.85 \times 10^{-6}\ s^{-1}$. Under these conditions, k_{obsd} for $(CO)_5MnCH_2OCH_3$ carbonylation was $(4.1 \pm 0.5) \times 10^{-6}\ s^{-1}$. Side-by-side experiments showed that **2** disappeared at the same rate *in the absence* of CO. Thus the observation of **2** → $(CO)_5MnCOCH_2I$ is precluded by the instability of the former.

The rate of carbonylation of $(CO)_5MnCH_3$ was much greater than that of **1**. Accurate rate constants could not be simultaneously determined for both compounds under identical conditions (solvent, temperature). In acetone-d_6 under 1000 psi of CO, k_{obsd} for $(CO)_5MnCH_3$ could be bounded as $\gtrsim 10$ times that of **1**.

Discussion

Silanes $(CO)_5MnSi(CH_3)_3$ and $(CH_3)_3SiI$ contrast in their reactivity toward formaldehyde. Both can be expected to silylate the carbonyl oxygen to give $H_2C{=}O^+{-}Si(CH_3)_3X^-$. When $X^- = I^-$, subsequent nucleophilic addition occurs. However, when $X^- = (CO)_5Mn^-$, formaldehyde polymerization appears to be faster than addition. Similar **3**/$(CH_3)_3SiI$ reactivity differences have been observed with other organic substrates.[20]

Silylated oxonium ions have been previously proposed as intermediates in $(CH_3)_3SiI$/methyl ether reactions,[14,15] and we likewise suggest the initially formed intermediate in eq 3 to be the ion pair **5**. However, attack of I^- upon the methyl group of **5**, which would irreversibly yield **1** analogously to the Jung–Olah demethylations, does not occur. Rather, dissociation of $CH_3OSi(CH_3)_3$ from **5** to give the methylidene $(CO)_5Mn^+{=}CH_2\ I^-$ (**6**; eq 3) is faster. Subsequent internal addition of I^- then affords product **2**. Direct S_N2 conversion of **5** to **2** is also possible, but in our opinion less likely.

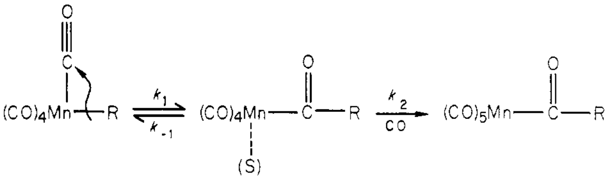
The carbonylation of manganese alkyls is known to occur via the two stage mechanism shown in eq 5.[2–7] The resulting rate expression

$$d[(CO)_5MnR]/dt = \frac{-k_1k_2[CO][(CO)_5MnR]}{k_{-1} + k_2[CO]}$$

simplifies when $k_2[CO] >> k_{-1}$ (a condition which for one study was met above 225 psi of CO)[4,21] to

$$d[(CO)_5MnR]/dt = -k_1[(CO)_5MnR]$$

Under these conditions, $k_{obsd} = k_1$ and thus reflects the migratory aptitude of the alkyl group (eq 5).



(5)

In the 750–1500-psi regime, $k_2[CO] >> k_{-1}$ for both **1** and $(CO)_5MnCH_2OCH_3$. Therefore the ratio of k_{obsd}, ca. 4, gives the $OSi(CH_3)_3/OCH_3$ substituent effect upon the rate of CH_2X migration. There are several obvious differences between $Si(CH_3)_3$ and CH_3: the former is much larger, more electropositive, and better able to stablize a β-positive charge[22] and increase its coordination number.[23] Apparently, these factors either do not significantly affect CH_2X migratory aptitudes, or they approximately cancel. When X = I, migration is slower yet. However, *in contrast to the example in eq 1*, carbonylation when X = H is considerably faster than when $X = OSi(CH_3)_3$.

In advance of this work, we considered several rationales as to why α-silyloxy and α-iodo substituents might cause anomalously high metal alkyl carbonylation rates. It is well-known that cation additives are important in optimizing glycol yields from CO/H_2 over rhodium catalysts.[24] Assocation of an electropositive atom M′ with a migrating CH_2O^- group might result in stabilized acyl **9**. However, our data do not provide any support for such an interaction involving silicon in **1** → **7**.

With **2**, it seemed possible that the iodide might anchimerically assist the alkyl migration mechanism via a weakly chelated intermediate such as **10**. We envisioned that iodide-promoted glycol synthesis[10] might occur similarly to the iodide promoted (rhodium catalyzed) $CH_3OH + CO \rightarrow CH_3CO_2H$ transformation.[25] As is well-known,

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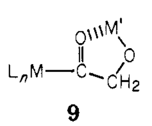

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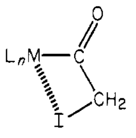

10

a key step in the latter is the conversion of kinetically unreactive CH_3OH to reactive CH_3I. However, our data show that the CH_2I group in 2 possesses no extraordinary migrating ability.

Cawse, Fiato, and Pruett found the k_{obsd} for carbonylation of $(CO)_5MnCH_2OCH_3$ at 30 °C in $CH_3CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_3$ to be $(2.5 \pm 0.4) \times 10^{-4}$ s^{-1}, which is quite close to the value we obtained in CH_3CN (25 °C).[3] These authors were also able to correlate the carbonylation rates of $(CO)_5MnCH_2CH_2CH_3$, $(CO)_5MnCH_2CH_3$, $(CO)_5MnCH_2(c\text{-}C_6H_{11})$, $(CO)_5MnCH_3$, and $(CO)_5MnCH_2C_6H_5$ to Taft CH_2X σ^* values (−0.115, −0.10, −0.06, 0.00, and +0.22, respectively) with a ρ^* of −8.8. Taft σ^* constants reflect polar/σ-inductive effects and are most positive with electron-withdrawing CH_2X groups.[26] While this correlation breaks down for groups with $\sigma^* > 0.30$ (such as CH_2OCH_3, $\sigma^* = 0.52$[3] − 0.64,[26] which migrates somewhat faster than expected), the reluctance of 2 to carbonylate ($\sigma^* = 0.85$ for CH_2I)[26] is nonetheless qualitatively predicted.

In summary, this study has provided useful new data on the carbonylation of manganese alkyls. The reactivity trend noted in eq 1 is not evidenced in the parent $(CO)_5MnCH_2X$ compounds and thus remains unexplained. We have considered the possibility that eq 1 might proceed via a different mechanism, but the carbonylation of related silyloxyalkyl $(CO)_5MnCH(n\text{-}C_3H_7)OSi(CH_3)_3$ with ^{13}CO showed the label distribution predicted by eq 5.[11b] Although the decomposition of 2 prevented the acquisition of quantitative data on its carbonylation rate, its chemistry will be the subject of future reports from our Utah laboratory.[1]

Experimental Section

General Data. All reactions and manipulations were carried out under an atmosphere of dry N_2. THF and ether were purified by distillation from benzophenone ketyl. Hexane was distilled from potassium. CH_2Cl_2 and CD_3CN were distilled from P_2O_5. $CDCl_3$ and CD_2Cl_2 were used without purification. "Ultra high purity" CO was obtained from Air Products and was used without purification or analysis.

IR spectra were recorded on a Perkin-Elmer Model 521 spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded (unless noted) at 200 and 50 MHz, respectively, on a Brüker WP-200 spectrometer, and were referenced to the deuterated solvent employed. Carbonylation rate measurements were made on a Varian T-60 spectrometer. Microanalyses were conducted by Galbraith Laboratories.

Starting Materials. $Mn_2(CO)_{10}$ was purchased from Pressure Chemical Co. and sublimed before use. $(CH_3)_3SiI$ was obtained from Petrarch Systems and was distilled from CaH_2 and stored over fine granular copper under N_2. Paraformaldehyde was purchased from Eastman. Internal standard $(C_6H_5)_3SiCH_3$ was synethesized from $(C_6H_5)_3SiCl$ and CH_3MgBr and recrystallized from CH_3OH.[27] Although $(CO)_5MnCH_2OCH_3$ is a known compound,[3,16] we were not able to find a literature preparation. We synthesized ours by the reaction of $K^+(CO)_5Mn^-$ (in THF)[28] with ICH_2OCH_3 (1.3 equiv; in ether)[29] at −78 °C. A white precipitate formed immediately, and after being stirred overnight at −30 °C, the reaction mixture was filtered through silica gel. The filtrate was concentrated to a dark yellow liquid and "sublimed" into a dry ice/CCl_4 cold finger to give $(CO)_5MnCH_2OCH_3$ (mp 3–5 °C) as a light yellow liquid in 40–50% yields.

Preparation of $(CO)_5MnCH_2OSi(CH_3)_3$ (1). Paraformaldehyde was predried by warming in vacuo for 5 h at 85 °C.[13] It was then pyrolyzed at 120 °C under vacuum, and the volatile products were collected in two cold traps. The first was cooled with dry ice and stopped water vapor, and the second was cooled with liquid nitrogen and collected solid formaldehyde monomer. When about 0.5 mL (ca. 13.6 mmol) of formaldehyde had collected, the system was filled with N_2 and a septum installed over the formaldehyde trap. Ether (which had been cooled to −78 °C) was then added to the formaldehyde trap via a transfer needle, and the resulting solution was then transferred into a −78 °C solution of $(CH_3)_3SiI$ (1.0 mL, 7.35 mmol) in 30 mL of ether. The resulting clear colorless solution turned cloudy upon sitting overnight at −30 °C. The mixture was then concentrated to ca. 10 mL under vacuum and added to a −78 °C solution of $K^+(CO)_5Mn^-$ (7.34 mmol)[28] in 30 mL of THF. A white precipitate formed immediately. The reaction was stirred for 1 h at −78 °C and then stored at −30 °C overnight. The reaction was cold filtered, and the resulting reddish brown solution was evaporated to dryness under vacuum while being maintained below 0 °C. The remaining liquid was "sublimed" onto an ice-cooled probe to give solid white 1 (1.45 g, 66% based upon $(CO)_5Mn^-$), mp 21.5–23 °C. Spectroscopic data: see Table I.

Preparation of $(CO)_5MnCH_2I$ (2). To $(CO)_5MnCH_2OCH_3$ (0.600 g, 2.50 mmol) in CH_2Cl_2 (30 mL) was added $(CH_3)_3SiI$ (0.45 mL, 3.25 mmol). After 45 min, the solution was filtered through silica gel and the solvent was removed under vacuum. The residue was sublimed at 40 °C under vacuum onto a ice-cooled cold finger. Yellow crystals of 2 (0.790 g, 2.35 mmol, 94%), mp 39.5–40.5 °C, were collected. Spectroscopic data: see Table I. Anal. Calcd for $C_6H_2IMnO_5$: C, 21.45; H, 0.60; I, 37.78; Mn, 16.35. Found: C, 21.55; H, 0.58; I, 37.48; Mn, 16.58.

Preparation of $(CO)_5MnCOCH_2OSi(CH_3)_3$ (7). A Fischer-Porter bottle was charged with 1 (0.149 g, 0.50 mmol) and ether (2 mL). It was then pressurized with 200 psi of CO. After 14 h, the pressure was released and the solvent was evaporated to give 0.162 g (0.49 mmol), 99%) of 7 as a white powder, mp 72.5–73.0 °C. Spectroscopic data: see Table I. Anal. Calcd for $C_{10}H_{11}MnO_7Si$: C, 36.82; H, 3.40; Mn, 16.84; Si, 8.61. Found: C, 36.73; H, 3.51; Mn, 16.77; Si, 8.76.

Carbonylation Rate Measurements. The following procedure was standard. To 0.60 mL of CD_3CN was added 0.20 mmol of $(CO)_5MnCH_2OCH_3$. To another 0.60 mL of CD_3CN was added 0.20 mmol of 1. These solutions were transferred to separate 10-mL volumetric flasks which contained a mini stir bar (surface area of solution, ca. 4 cm^2). The two flasks were placed in a 1-L stainless-steel autoclave. Some Nujol was added to the bottom of the autoclave interior to enhance temperature stability. The autoclave was pressurized to 700–1500 psi, and the solutions were stirred via an external stir plate. Data points were taken at ca. 5-min intervals by discharging the autoclave and transferring the solutions to NMR tubes (k_{-1} negligible). Product and starting material methylene resonances were integrated ($(CO)_5MnCH_2OCH_3$, δ 4.21; $(CO)_5MnCOCH_2OCH_3$, δ 3.78). The NMR samples were returned to the autoclave, and fresh CD_3CN was added (to compensate for evaporative losses) to maintain the initial volume of 0.60 mL.

Decomposition and Attempted Carbonylation of 2. To 1.00 mL of CH_2Cl_2 was added 0.20 mmol of 2 and 0.055 g (0.20 mmol) of internal standard $(C_6H_5)_3Si(CH_3)$. To another 1.00 mL of CH_2Cl_2 was added 0.20 mmol of $(CO)_5MnCH_2OCH_3$. These were treated at 24 °C with 1300 psi of CO as described in the previous experimental procedure. Starting material concentrations were determined by ^1H NMR integration of the CH_2 protons at 0.5, 5.0, 36, and 74 h. A similar experiment was conducted in CD_3CN under 750 psi of CO. Data: see Results.

To 0.60 mL of CH_3CN was added 0.061 g (0.18 mmol) of $(CO)_5MnCH_2I$. This solution was treated with 1200 psi of CO

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for 18 h as described in the previous experimental. The solvent was blown off with N_2 to yield 0.58 mg of an orange solid. The solid was vacuum sublimed to give 0.050 g (0.16 mmol, 87%) of crystalline $(CO)_5MnI$ (IR (hexane, cm^{-1}) 2131 (w), 2050 (s), 2009 (m)) which was identical with an authentic sample[30] by TLC.

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Photoelectron Spectroscopy of f-Element Organometallic Complexes. 5. Comparative Study of Ring-Substituted Uranocenes

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This paper presents the first data obtained on the electronic structure of 1,1′-ring-substituted uranocenes studied by He I and He II photoelectron spectroscopy. Quite unexpectedly, differences of the electron donor–acceptor properties of substituents do not result in any significant change of spectral patterns, the photoelectron data thus pointing to the same bonding model adopted for the unsubstituted complex. Ring substitution leads to the lifting of degeneracy of π orbitals in the electroneutral free ligand. By contrast similar effects, due to the lowering of the symmetry, are not evident in the spectra of 1,1′-ring-substituted complexes neither in the form of splitting nor broadening of ligand-centered photoelectron bands. Within the proposed molecular orbital model, this observation is evidence of comparable involvement of U 5f and U 6d orbitals in the metal–ligand bonding. The values associated with ionizations of ligand-centered π molecular orbitals in the ring-substituted uranocenes do not depend upon the nature of a particular substituent. This observation suggests an almost unique ability of the central uranium atom to restore electronic charge variation induced on the ligand.

Introduction

Great efforts in recent years devoted to an understanding of the metal–ligand bonding in actinoid organometallics have resulted in a revision of some aspects of the bonding model previously adopted.[1] Thus the photoelectron (PE) spectra of the highly symmetrical cyclooctatetraenide complexes, $An(C_8H_8)_2$ (An = Th(IV), U(IV)), have provided evidence of a substantial participation of 6d as well as 5f orbitals in the bonding,[2] and analogous conclusions have been arrived at by high-level theoretical calculations.[3] In the case of actinide complexes of considerably lower symmetry, the use of combined He I and He II PE techniques as well as the comparison with the spectra of analogous *n*d transition-metal complexes have indicated specific metal–ligand covalency effects due not only to 5f metal subshells but also to 6d orbitals as well.[4,5]

In order to gain a further insight into the problem, we have extended our research on the bonding in actinoid sandwich compounds to the PE spectra of two 1,1′-ring-substituted uranocene derivatives, namely, $U(C_8H_7R)_2$ (R = $Si(CH_3)_3$, $P(t\text{-}C_4H_9)_2$.

Another motivation for this study has been the expectation of a substantial perturbation of the ligand electronic structure by the ring substituent which should allow an estimate as to what extent the resulting spectral variations fit into the framework of the current bonding hypotheses.

Experimental Section

The complexes under study were purified by vacuum sublimation and always handled under argon atmosphere. Spectra were run on a Perkin-Elmer PS 18 spectrometer modified by inclusion of a hollow cathode discharge lamp giving high yields of He II photons. Energy calibration of spectra was obtained by reference to peaks of Ar and Xe gases allowed into the target chamber and to He ls^{-1} self-ionization. Spectra were run in the 100–120 °C temperature range.

Results and Discussion

Figure 1a shows the PE spectrum of the electroneutral ligand $C_8H_7Si(CH_3)_3$, which is of some relevance to the understanding of the spectrum of its uranium complex, $(C_8H_7Si(CH_3)_3)_2U$ (hereafter U(cotSi)$_2$). The general ap-

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