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Transition-metal sulfur ylide complexes. 23. Methylene transfer from sulfur ylides to transition-metal complexes: a parallel between sulfur ylides and diazomethane to organometallic chemistry

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electric dipole transitions only. In principle, magnetic dipole transitions cannot be ruled out either, but according to all present experience with noncentrosymmetric uranium(IV) systems, their magnetic dipole transitions are by at least 1 order of magnitude weaker than forced electric dipole transitions.[26] The above treatment of various organouranium(IV) systems $[Cp_3UX_2]^q$ seems to provide for the first time[27] a sufficiently large, purely experimental basis for a promising CF analysis with the final aim to arrive at a better understanding of the still unsolved electronic structure of Cp_3U^{IV} derivatives. It is hoped to end up in the near future at CF parameter sets which may be optimally correlated with predictions from recently elaborated, purely theoretical treatments.[28]

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Registry No. **1**, 103533-67-1; **2**, 84517-79-3; **3**, 89014-39-1.

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(26) See: Satten, R. A.; Schreiber, C. L.; Wong, E. Y. *J. Chem. Phys.* **1965**, *42*, 162. Nevertheless, in view of the well-established magnetic dipole character of the transition $\Gamma_1(^3H_4) \rightarrow \Gamma_4(^3H_5)$ of Cs_2UX_6 (X = Cl, Br) around 6.300 cm^{-1}, some uncertainty remains for the correct nature of transition 2 in Figures 3 and 4.

(27) We are aware of an earlier, albeit essentially purely descriptive MCD study of uranocene, $(\eta^8\text{-}C_8H_8)_2$UIV, the f–f absorption spectrum of which is, due to the high molecular symmetry, strongly dominated by vibronic satellites: Mowrey, R. L. Ph.D Thesis, University of Virginia, 1976.

(28) Tatsumi, K.; Nakamura, A. *J. Organomet. Chem.* **1984**, *272*, 141. Tatsumi, K., personal communication.

(29) **Note added in proof**: Preliminary CF calculations indicate that bands 3 of **1** and 2 of **2** and **3** have to be ascribed to the transition $\Gamma_1(^3H_4) \rightarrow \Gamma_6$, whereas bands 2 of **1** and 3 of **2** and **3** should correspond to the transition $\Gamma_1(^3H_4) \rightarrow \Gamma_4$. The calculated *g* value of the Γ_6 level would lead to a positive Faraday *A* term as found for **2** and **3**, but not for **1**.

Transition-Metal Sulfur Ylide Complexes. 23.[1] Methylene Transfer from Sulfur Ylides to Transition-Metal Complexes: A Parallel between Sulfur Ylides and Diazomethane in Organometallic Chemistry

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Treatment of $(\eta^5\text{-}C_5H_4R^1)Mn(CO)_2(THF)$ (R^1 = H, Me) with $(Me_2N)(R^2)S(O){=}CH_2$ (R^2 = Me, Ph) in THF afforded the μ-alkylidene complexes $[(\eta^5\text{-}C_5H_4R^1)(CO)_2Mn]_2CH_2$(*Mn–Mn*) and the ethylene complexes $(\eta^5\text{-}C_5H_4R^1)Mn(CO)_2(C_2H_4)$. With $(C_5Me_5)Mn(CO)_2(THF)$ only the ethylene complex was obtained. The mechanism of the transformations is discussed in comparison to the related reactions between the manganese tetrahydrofuran complexes with diazomethane.

Introduction

An ylide complex can be described as a base-stabilized carbene complex.[2] Thus the stability of ylide complexes of

$$L_nM \leftarrow CH_2 \leftarrow ER_n$$

the general type $L_nMCH_2ER_n$ increases with the growing nucleophilicity of the component ER_n and the electron-attracting capability of the transition-metal fragment L_nM.

The reaction of $(CO)_5Cr(CH_2PR_3)$ with tertiary phosphines PR'_3 led to CO displacement,[3] whereas sulfur ylide complexes $(CO)_5Cr[CH_2S(O)R^2R^3]$ were converted to phosphonium ylide complexes when treated with PR_3.[4] This is rationalized by the inferior donor capacity of a sulfide or sulfoxide in comparison to a phosphine. A kinetic study of the aforementioned reaction revealed that $(CO)_5Cr[CH_2S(O)Me_2]$ underwent irreversible dissociation into dimethyl sulfoxide and the very reactive carbene complex $(CO)_5Cr{=}CH_2$ which is subsequently trapped by phosphines.[5]

$$(CO)_5Cr[CH_2S(O)Me_2] \xrightarrow[-Me_2SO]{} [(CO)_5Cr{=}CH_2] \xrightarrow{+ER_3} (CO)_5Cr[CH_2ER_3]$$

Such a dissociation process should be markedly facilitated when the leaving group tendency of the sulfide component of the sulfur ylide is enhanced as compared to dimethylsulfoxide. Moreover, the generation of a carbene species seems more likely with electron-rich transition-metal fragments which provide additional stabilization to the electron-deficient carbene ligand.[6] In an extreme view it should be possible to generate stable carbene (methylene) complexes from electron-rich metal complexes and stable sulfur ylides.[7]

Here we report on our studies of the reactivity of complexes $(\eta^5\text{-}C_5H_4R^1)(CO)_2Mn(THF)$ (R^1 = H,[8] Me[8]) and

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(1) For part 22, see: Weber, L. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1985**, *B40*, 373.

(2) For reviews see: (a) Weber, L. In The Chemistry of the *Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: Chichester, 1982; p 91. (b) Weber, L. *Angew. Chem.* **1983**, *95*, 539; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 516. (c) Schmidbaur, H. *Angew. Chem.* **1983**, *95*, 980; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907. (d) Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1.

(3) Knoll, L. *J. Organomet. Chem.* **1979**, *182*, 77.

(4) Weber, L. *J. Organomet. Chem. 141*, 1977, 49.

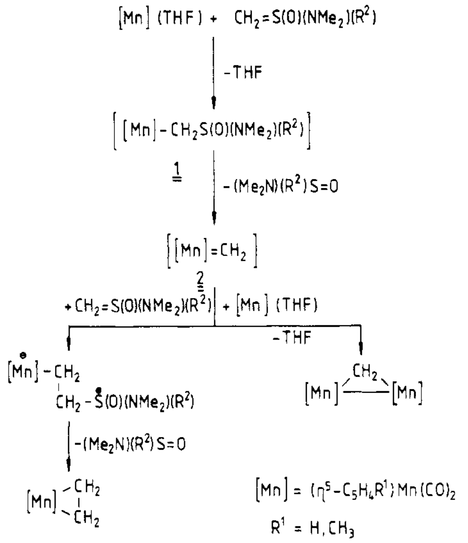
(5) Fischer, H.; Weber, L. *Chem. Ber.* **1984**, *117*, 3340.

(6) For stable $Re{=}CH_2$ complexes see for example: Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804 and references cited herein.

(7) Recently Gladysz demonstrated the reversible formation of the sulfur ylide complex $[(C_5H_5)(NO)(PPh_3)Re\text{-}CH_2SMe_2]^+$ by the addition of Me_2S to the cation $[(C_5H_5)(NO)(PPh_3)Re{=}CH_2]^+$: McCormick, F. B.; Gladysz, J. A. *J. Organomet. Chem.* **1981**, *218*, C57.

0276-7333/86/2305-2114$01.50/0

Scheme I. Proposal for the Mechanism of Formation of μ-Methylidene and Ethylene Complexes from Sulfur Ylides and $(C_5H_4R^1)(CO)_2Mn(THF)$



$(\eta^5\text{-}C_5Me_5)(CO)_2Mn(THF)$[9] toward the sulfur ylides $Me_2S(O){=}CH_2$[10] and $(Me_2N)(R^2)S(O){=}CH_2$ (R^2 = Me,[11] Ph[12]). When a photochemically prepared solution of $(MeC_5H_4)(CO)_2Mn(THF)$ is treated with half the molar amount of $Me_2S(O){=}CH_2$, the wine-red solution slowly turns brown. The IR spectrum of the solution does not show ν(CO) bands in the region typical for dicarbonyl cyclopentadienyl manganese ylide complexes (1804–1795 cm^{-1}).[13] After removal of solvent and volatiles in vacuo, the carbonyl-containing components are extracted into hexane. Slow concentration and cooling of the solution gives light yellow $(Me\ C_5H_4)(CO)_2Mn(Me_2SO)$[14] in ca. 35% yield. Chromatographic workup of the mother liquor affords yellow oily $(MeC_5H_4)(CO)_2Mn(C_2H_4)$[15] in 56% yield and only traces of $[(MeC_5H_4)(CO)_2Mn]_2CH_2$(*Mn-Mn*).[15] When the same reaction is carried out with the sulfur ylides $(Me_2N)(Me)S(O) = CH_2$[11] and $(Me_2N)(Ph)S(O){=}CH_2$[12] which are based on the less nucleophilic sulfinic amides $Me_2NS(O)Me$ and $Me_2NS(O)Ph$, no sulfinic amide complexes such as $(MeC_5H_4)(CO)_2Me[Me_2NS(O)R]$ are obtained. Instead the yield of the bridged alkylidene complex increases to 30–44%. The amount of ethylene complex formed ranges from 16 to 41%. If the ratio of the THF complex to ylide is varied from 2:1 to 6:1, the alkylidene complex becomes the predominant product (75%, accompanied by only 21% of ethylene complex). On the other hand a fourfold excess of sulfur ylide suppresses the formation of $[MeC_5H_4)(CO)_2Mn]_2CH_2$(*Mn-Mn*) completely in favor of the ethylene complex (66%).

The analogous compound $(C_5H_5)Mn(CO)_2(THF)$ undergoes comparable transformations when treated with the dimethylamino-substituted ylides in a ratio of 2:1. With $(C_5Me_5)(CO)_2Mn(THF)$ and $(Me_2N)(Ph)S(O){=}CH_2$ only the ethylene complex is obtained. A rationale for these findings is given in Scheme I.

In the first step of the reaction an ylide complex, 1, is formed. In contrast to the related phosphorus ylide complexes such as $(C_5H_4R)(CO)_2Mn(CH_2PMe_3)$, and $(C_5H_4R)(CO)_2Mn(CH_2PPh_3)$[13] compound 1 is unstable, and the sulfinic amide $(Me_2N)R^2S{=}O$ rapidly dissociates.[16] The resulting carbene complex 2 is not sufficiently stable to be isolated or to be observed by spectroscopic means. However, it is efficiently trapped by an excess of the THF complex $(C_5H_4R)(CO)_2Mn(THF)$ to give the bridging methylene complex. With a sixfold excess of the THF complex, this is the principal route of reaction. On the other hand, when an excess of ylide is present, the electrophilic center at the carbene ligand is attacked by the nucleophilic ylide to give a betaine which is stabilized by loss of the good leaving group $(Me_2N)(R^2)S{=}O$, yielding the ethylene complex. Precedence for this type of reaction is the conversion of $(CO)_5W{=}C(OMe)Ph$ to a vinyl ether and $(CO)_5W(PPh_3)$ by treatment with the Wittig ylide $Ph_3P{=}CH_2$.[17]

These results are remarkable for several reasons. 1. It is demonstrated that sulfur ylides and diazoalkanes not only correspond in their organic chemistry (e.g., epoxidation, cyclopropanation)[18] but also exhibit similar reactivities toward organometallics.[19] 2. Our results clearly show that in addition to diazomethane, sulfur ylides are also useful precursors for the introduction of a μ-methylidene ligand.[20] 3. In contrast to diazomethane, which can be regarded as a nitrogen ylide, $H_2C{=}N_2$, with the N_2-leaving group, the nucleophilicity of sulfur ylides can be fine-tuned by the proper choice of the sulfide. In principle, better selectivities are expected when sulfur ylides are used instead of the hazardous diazomethane.

The transfer of alkylidene groups from sulfur ylides to other organometallics is under active investigation in our laboratory.

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. Ultraviolet irradiations were performed in a water-cooled photoreactor (Hanovia 150-W mercury lamp). Infrared spectra were recorded on a Perkin-Elmer Model 597 spectrometer. The ^1H NMR spectra were taken on a Varian XL 200 NMR spectrometer ($SiMe_4$ standard). Electron-impact mass spectra were recorded on a Varian MAT 312 spectrometer. Elemental

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analyses were obtained from the Microanalytical Laboratory of the University Essen.

Materials. The sulfur ylides $Me_2S(O){=}CH_2$,[10] $(Me_2N)(Me)S(O){=}CH_2$[11] and $(Me_2N)(Ph)S(O){=}CH_2$[10] as well as the complex $(C_5Me_5)Mn(CO)_3$[9] were prepared as described in the literature. $(C_5H_5)Mn(CO)_3$ and $(MeC_5H_4)Mn(CO)_3$ were purchased from Strem Chemicals. Silica gel 60 (70–230 mesh ASTM, Merck) was used for column chromatography ($l = 70$ cm; $\phi = 2.5$ cm). All solvents were rigorously dried with an appropriate drying agent and distilled prior to use. All compounds obtained in this study were identified by comparison with authentic samples (IR, ^1H NMR, MS, melting point). Yields are based on the amount of ylide employed if not stated otherwise.

Reaction of $(MeC_5H_4)Mn(CO)_2(THF)$ with $Me_2S(O){=}CH_2$. A solution of 1.380 g (6.33 mmol) of $(MeC_5H_4)Mn(CO)_3$ in 200 mL of THF was irradiated for 2 h at 0 °C. To the resulting wine-red solution of $(MeC_5H_4)Mn(CO)_2(THF)$ was added 5 mL of a 0.6 M THF solution of $Me_2S(O){=}CH_2$ (3.00 mmol) dropwise with vigorous stirring. After 1.5 h the brown solution was freed from solvents and volatiles in vacuo. The oily residue was extracted with 100 mL of hexane. Concentration of the filtrate to about 30 mL and cooling at −15 °C resulted in the precipitation of light yellow $(MeC_5H_4)Mn(CO)_2(Me_2SO)$ (0.279 g, 35%): mp 64–66 °C (lit.[14] 65 °C); IR (*n*-hexane) 1954 s, 1892 s cm^{-1} (ν(CO)); IR (Nujol) 1070 s cm^{-1} (ν(S=O)). Anal. Calcd for $C_{10}H_{13}MnO_3S$ (268.2): C, 44.78; H, 4.89. Found: C, 44.73; H, 5.01.

The red mother liquor was evaporated to dryness and the residue chromatographed on silica gel. Development with petroleum ether gave two yellow bands and one red-brown band. The first yellow band contained unreacted $(MeC_5H_4)Mn(CO)_3$ whereas from the second yellow band 0.182 g (56%) of $(MeC_5H_4)Mn(CO)_2(C_2H_4)$ was isolated: IR (*n*-hexane) 1970 s, 1913 s cm^{-1} (ν(CO)) (lit.[15] 1972 s, 1913 s cm^{-1}); ^1H NMR (C_6D_6, 22 °C) δ 1.45 (s, 3 H, $CpCH_3$), 1.99 (s, 4 H, C_2H_4), 3.80 (m, 4 H, C_5H_4) (lit.[14] (C_6D_6) δ 1.43 (s, 3 H, $CpCH_3$), 1.97 (s, 4 H, C_2H_4), 3.88 (m, 4 H, C_5H_4).

The red-brown band was eluted with a mixture of benzene/petroleum ether (1:9) to give 0.005 g of $[(MeC_5H_4)(CO)_2Mn]_2CH_2$(*Mn–Mn*).

Reaction of $(MeC_5H_4)Mn(CO)_2(THF)$ with $(Me_2N)(Ph)S(O){=}CH_2$ (2:1). As described a solution of 2.616 g (12.0 mmol) of $(MeC_5H_4)Mn(CO)_3$ in 350 mL of THF was converted into the THF complex and then treated with 32 mL of 0.19 M THF solution of $(Me_2N)(Ph)S(O){=}CH_2$ (6.1 mmol). The reaction was monitored by IR spectroscopy of the brown solution. When the ν(CO) band of the THF complex at 1848 cm^{-1} decreased to $^1/_5$ of its original intensity, solvents were removed in vacuo. Analogous workup afforded 0.270 g (41%) of $(MeC_5H_4)Mn(CO)_2(C_2H_4)$ and 0.804 g (34%) of $[(MeC_5H_4)(CO)_2Mn]_2CH_2$(*Mn–Mn*): IR (*n*-hexane) 1969 w, 1943 vs, 1913 vs, 1898 sh cm^{-1} (lit.[15] 1973 w, 1942 vs, 1912 vs, 1896 w cm^{-1}); ^1H NMR (C_6D_6, 22 °C, internal Me_4Si standard) δ 1.58 (s, 6 H, CH_3), 4.02–4.27 (m, 8 H, C_5H_4), 8.61 (s, 2 H, CH_2) (lit.[15] (C_6D_6) δ 1.84 (s, 6 H), 4.4 (m, 8 H), 8.82 (s, 2 H)); MS/CI found 394 (M^+).

Reaction of $(MeC_5H_4)Mn(CO)_2(THF)$ with $(Me_2N)(Me)S(O){=}CH_2$ (2:1). Analogously 0.086 g (16%) of $(MeC_5H_4)Mn(CO)_2(C_2H_4)$ and 0.587 g (30%) of $[(MeC_5H_4)(CO)_2Mn]_2CH_2$(*Mn–Mn*) were obtained from the reaction of $(MeC_5H_4)Mn(CO)_2(THF)$ (prepared from 2.180 g (10.0 mmol) of $(MeC_5H_4)Mn(CO)_3$) and 0.606 g (5.0 mmol) of $(Me_2N)(Me)S(O){=}CH_2$ in 350 mL of THF.

Reaction of $(MeC_5H_4)Mn(CO)_2(THF)$ with $(Me_2N)(Ph)S(O){=}CH_2$ (1:4). A solution of 1.431 g (6.6 mmol) of $(MeC_5H_4)Mn(CO)_3$ in 350 mL of THF was photochemically converted into the THF complex, which was reacted with 132 mL (26.4 mmol) of a 0.2 M THF solution of $(Me_2N)(Ph)S(O){=}CH_2$. The usual workup afforded 0.912 g (63% relative to $(MeC_5H_4)Mn(CO)_3$) of $(MeC_5H_4)Mn(CO)_2(C_2H_4)$. No alkylidene complex was obtained.

Reaction of $(MeC_5H_4)Mn(CO)_2(THF)$ with $(Me_2N)(Ph)S(O){=}CH_2$ (6:1). The THF complex, photochemically generated from 2.617 g (12.0 mmol) of $(MeC_5H_4)Mn(CO)_3$, was treated with 10 mL of a 0.2 M THF solution of $(Me_2N)(Ph)S(O){=}CH_2$ (2.0 mmol) to yield 0.591 g (75%) of $[(MeC_5H_4)(CO)_2Mn]_2CH_2$(*Mn–Mn*) and 0.047 g (21.5%) of $(MeC_5H_4)Mn(CO)_2(C_2H_4)$.

Reaction of $(C_5H_5)Mn(CO)_2(THF)$ with $(Me_2N)(Ph)S(O){=}CH_2$ (2:1). A solution of 2.274 g (11.1 mmol) of $(C_5H_5)Mn(CO)_3$ in 350 mL of THF was irradiated for 2 h at 0 °C and subsequently treated with 25 mL of a 0.2 M THF solution of $(Me_2N)(Ph)S(O){=}CH_2$ (5.0 mmol). Usual workup furnished 0.176 g (35%) of $(C_5H_5)Mn(CO)_2(C_2H_4)$ [IR (hexane) 1973 vs, 1913 vs cm^{-1} (ν(CO)) (lit.[15] 1975 vs, 1916 vs cm^{-1}); ^1H NMR (C_6D_6, 22 °C) δ 1.97 (s, 4 H, C_2H_4), 3.79 (s, 5 H, Cp) (lit.[15] δ 2.02 (s, 4 H), 3.83 (s, 5 H)); MS/CI found 204 (M^+)] and 0.337 g (18%) of $[(C_5H_5)(CO)_2Mn]_2CH_2$(*Mn–Mn*) [IR (*n*-hexane) 1977 w, 1949 vs, 1919 vs, 1902 w cm^{-1} (lit.[15] 1978 w, 1949 vs, 1919 vs, 1902 w cm^{-1}); ^1H NMR (C_6D_6, 22 °C) δ 4.12 (s, 10 H, Cp), 8.68 (s, 2 H, CH_2) (lit.[15] δ 4.13 (s, 10 H), 8.65 (s, 2 H); MS/CI found 366 (M^+)].

Reaction of $(C_5H_5)Mn(CO)_2(THF)$ with $(Me_2N)(Me)S(O){=}CH_2$ (2:1). Analogously the wine-red THF solution of the THF complex (prepared from 2.043 g (10.0 mol) of $(C_5H_5)Mn(CO)_3$) reacted with 0.606 g (5.0 mmol) of $(Me_2N)(Me)S(O){=}CH_2$ to give 0.184 g (36%) of $(C_5H_5)Mn(CO)_2(C_2H_4)$ and 0.212 g (12%) of $[(C_5H_5)(CO)_2Mn]_2CH_2$(*Mn–Mn*).

Reaction of $(C_5Me_5)Mn(CO)_2(THF)$ and $(Me_2N)(Ph)S(O){=}CH_2$ (1:1). A solution of 2.900 g (10.6 mmol) of $(C_5Me_5)Mn(CO)_3$ in 300 mL of THF was photochemically converted into the corresponding THF complex and subsequently allowed to react with 37 mL of a 0.29 M THF solution of $(Me_2N)(Ph)S(O){=}CH_2$. The usual workup yielded 1.050 g (83%) of yellow $(C_5Me_5)Mn(CO)_2(C_2H_4)$.[21]

Acknowledgment. This work has been generously supported by the Deutsche Forschungsgemeinschaft (Bonn) and the Fonds der Chemischen Industrie (Frankfurt), which are gratefully acknowledged.

Registry No. $(MeC_5H_4)Mn(CO)_2(THF)$, 51922-84-0; $Me_2S(O){=}CH_2$, 5367-24-8; $(MeC_2H_4)Mn(CO)_3$, 12108-13-3; $(MeC_2H_4)Mn(CO)_2(Me_2SO)$, 66060-31-9; $(MeC_5H_4)Mn(CO)_2(C_2H_4)$, 57603-43-7; $[(MeC_5H_4)(CO)_2Mn]_2CH_2$(*Mn–Mn*), 57603-42-6; $(Me_2N)(Ph)S(O){=}CH_2$, 30004-64-9; $(Me_2N)(Me)S(O){=}CH_2$, 38709-75-0; $(C_5H_5)Mn(CO)_3$, 12079-65-1; $(C_5H_5)Mn(CO)_2(C_2H_4)$, 12108-31-5; $(C_5H_5)Mn(CO)_2THF$, 12093-26-4; $[(C_5H_5)(CO)_2Mn]_2CH_2$(*Mn–Mn*), 57603-41-5.

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