the downfield resonances at δ 283 and 282 in the $^{13}C\{^1H\}$NMR spectrum, is consistent with some carbenoid resonance contribution to the ground state of **1-Mn**.

The combination of a stereogenic metal center and activated hydrogens holds promise for asymmetric induction in the alkylation chemistry of **1**. When **1-Re** is deprotonated with LDA at −78 °C, warmed to 0 °C, and treated with CH_3I, C-alkylation product **3** is obtained as an orange solid (69%)[5] (Scheme I). Isolated **3** exists as a single diastereomer by ^1H NMR spectroscopy; however, we are unable to assign stereochemistry on the basis of spectroscopic data.

In a similar manner, deprotonation of **1-Re** with LDA and addition of trimethylsilyl chloride generates O-silylation product **4** as an orange solid (74%).[5] This result is in sharp contrast to silylation of simple metallaenolate anions such as **2**[9] and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_2Li)$ (**5**),[10] for which only C-silylation is observed. In addition to electronic factors, as described by Davies for **5**,[10] steric factors may contribute to this contrasting silylation chemistry.[11]

The mechanism for μ-malonyl formation appears to involve attack of the enolate anion directly at a terminal carbonyl ligand in $(CO)_5M(OSO_2CF_3)$. To our knowledge this chemistry represents new modes of reactivity for both metallaenolate[12] and metal carbonyl triflate complexes.[13] We are currently examining the generality of this entry into μ-malonyl complexes as well as the further reactivity of these novel compounds with respect to asymmetric carbon–carbon bond formation and metal-catalyzed carbon monoxide chemistry.

Acknowledgment. Partial support from Research Corp. and the Academic Senate at the University of California, San Diego, as well as helpful discussions with Professors W. C. Trogler and J. A. Gladysz are gratefully acknowledged.

Registry No. 1-Re, 109801-58-3; 1-Mn, 109801-59-4; 2, 109801-57-2; 3, 109801-60-7; 4, 109838-66-6; $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(COCH_3)$, 99901-55-0; $(CO)_5Re(OSO_2CF_3)$, 96412-34-9; $(CO)_5Mn(OSO_2CF_3$, 89689-95-2.

Supplementary Material Available: Listings of fractional coordinates, bond distance, bond angles, hydrogen atom coordinates, thermal parameters, and full analytical and spectroscopic characterization of all new compounds (7 pages); a listing of structure factors (40 pages). Ordering information is given on any current masthead page.

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[8] (a) For comparison: $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)[CH(C_6H_5)(CH_2C_6H_5)]$, 2.215 (4) Å; $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHC_6H_5)]^+PF_6^-$, 1.949 (6) Å;[8b] $Ph_2PCH_2CH_2(O)CMn(CO)_2(dppm)$, 2.207 (6) Å;[8c] $Mn({=}CO(CH_3)(OEt))(CO)_4(CH_2C_6H_5\text{-}1\text{-}NpGe)$, 1.951 (20) Å.[8d] (b) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. (c) Carriedo, G. A.; Parra Soto, J. B.; Riera, V.; Solans, X.; Miravitlles, C. *J. Organomet. Chem.* **1985**, *297*, 193. (d) Carre, F.; Cerveau, G.; Colomer, E.; Corriu, R. J. P. *J. Organomet. Chem.* **1982**, *229*, 257.

[9] Reaction of 2 and TMSCl results in clean C-silylation: O'Connor, J. M.; Uhrhammer, R., unpublished observation.

[10] Aktogu, N.; Felkin, H.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1982**, 1303.

[11] In the enolate anion derived from **1-Re**, the oxygen atom is sterically accessible. In **2** and **5**, ON–Re–C_α–O and OC–Fe–C_a–O torsion angles of ~180° would place oxygen in a more sterically congested environment than carbon.[4,7]

[12] For the use of metallaenolates for preparation of bimetallic complexes, see: (a) Ho, S. C. H.; Straus, D. A.; Armantrout, J.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2210. (b) Akita, M.; Kondoh, A. *J. Organomet. Chem.* **1986**, *299*, 369. (c) Weinstock, I.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1986**, *108*, 8298.

[13] (a) Schmidt, S. P.; Basolo, F.; Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 1894. (b) Schmidt, S. P.; Nicschke, J.; Trogler, W. C. *Inorg. Synth.*, in press.

Transition-Metal-Substitued Diphosphenes. 10.[1] Reaction of the Diphosphenyl Complex $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}PAr$ (Ar = 2,4,6-*t*-$Bu_3C_6H_2$) with Sulfur and Selenium. Preparation and X-ray Structure Analysis of the First Phosphinidene(thioxo)phosphoranyl Complex $(\eta^5\text{-}C_5Me_5)(CO)_2FeP({=}S){=}PAr$

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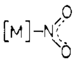
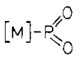
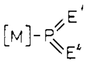
Summary: The reaction of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}PAr$ with sulfur and selenium in THF at 20 °C afforded the novel complexes $(\eta^5\text{-}C_5Me_5)(CO)_2FeP({=}E){=}PAr$ with a ligand formally derived from the metaphosphite ion PO_2^-. Only the sulfur derivative appeared to be stable at ambient temperature, whereas the selenium compound in solution slowly rearranged to the selenadiphosphiranyl complex $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{P\text{-}Se\text{-}P}Ar$. The structure of the sulfur derivative was established by a single-crystal X-ray diffraction study.

Compounds featuring multiple bonds between heavier main-group elements are attracting significant continued attention.[2] Transition-metal complexes containing the nitro ligand (A) belong to the classical Werner-type complexes.


A


B


C

E',E''= S,Se, NR,PR

On the other hand, coordination compounds of the homologous metaphosphite ligand (B) or derivatives thereof (C) have not been described in the literature until now. Recently we published the synthesis and molecular structure of transition-metal-substitued diphosphenes (diphosphenyl complexes).[3] Here we report on the first phosphinidene(thioxo)phosphoranyl complex, which formally is a member of compounds of class C, and on the first examples of thiadiphosphiranes and selenadiphosphiranes functionalized by organometallic fragments.[4]

Equimolar amounts of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}PAr$ (**1**) (Ar = 2,4,6-*t*-$Bu_3C_6H_2$) and sulfur were allowed to react in tetrahydrofuran solution at 20 °C.[5] From the reaction

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[1] For part 9, see: Weber, L.; Reizig, K.; Bungardt, D.; Boese, R. *Chem. Ber.*, in press.

[2] For reviews see: (a) Cowley, A. H. *Polyhedron* **1984**, *3*, 389. (b) Scherer, O. J. *Angew. Chem.* **1985**, *97*, 905; *Angew. Chem., Int. Ed. Engl.* **1986**, *24*, 924.

[3] Weber, L.; Reizig, K.; Bungardt, D.; Boese, R. *Organometallics* **1987**, *6*, 110.

[4] Various diphosphenes have been oxidized by sulfur. (a) Yoshifuji, M.; Shibayama, K.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Chem. Soc., Chem. Commun.* **1983**, 862. (b) Yoshifuji, M.; Shibayama, K.; Inamoto, N. *Heterocycles* **1984**, *22*, 681. (c) Escudie, J.; Couret, C.; Ranaivonjatovo, H.; Satge, J. *Phosphorus Sulfur* **1983**, *17*, 22. (d) Niecke, E.; Rüger, R. *Angew. Chem.* **1983**, *95*, 154; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 155. Various diphosphenes have been oxidized by selenium. Yoshifuji, M.; Inamoto, N. *Chem. Lett.* **1984**, 603.

0276-7333/87/2306-1989$01.50/0

Table I. Selected Bond Lengths (Å) and Angles (deg) for 2

Bond Lengths			
Fe-P(1)	2.227 (1)	P(1)-S	1.936 (2)
Fe-C(1)	1.771 (4)	C(1)-O(1)	1.134 (5)
Fe-C(2)	1.770 (5)	C(2)-O(2)	1.135 (6)
P(1)-P(2)	2.041 (1)	P(2)-C(3)	1.885 (3)
Bond Angles			
P(1)-Fe-C(1)	89.9 (1)	P(2)-P(1)-S	124.4 (1)
P(1)-Fe-C(2)	89.8 (2)	P(1)-P(2)-C(3)	104.8 (1)
C(1)-Fe-C(2)	95.2 (2)	Fe-C(1)-O(1)	177.3 (4)
Fe-P(1)-P(2)	114.2 (1)	Fe-C(2)-O(2)	176.7 (4)
Fe-P(1)-S	121.2 (1)		

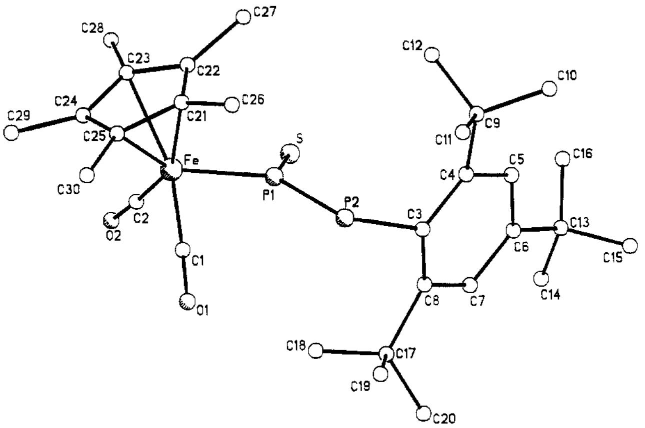
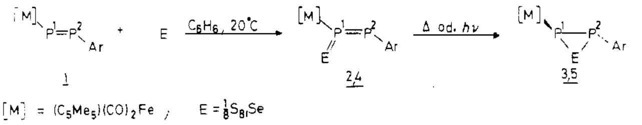


Figure 1. Molecular structure of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP({=}S){=}PAr$ (2).

mixture red crystalline $(\eta^5\text{-}C_5Me_5)(CO)_2FeP({=}S){=}PAr$ (**2**) was isolated. Heating a solution of this compound in benzene (80 °C, 2 h) led to the thiadiphosphiranyl complex **3** which was purified by column chromatography (Florisil). The sulfurization as well as the rearrangement were monitored by ^{31}P NMR spectroscopy. Two doublets of **1** at δ 715.2 and 553.5 ($^1J_{PP}$ = 594.2 Hz) were found shifted considerably upfield in **2** at δ 398.0 and 295.0 ($^1J_{PP}$ = 618.5 Hz). Thiadiphosphirane formation was accompained by additional upfield shifts of $\Delta\delta$ = 314.1 ppm for the iron bonded atom P1 and 385.3 ppm for the organic-substituted atom P2, and the coupling constant was decreased by 385.9 Hz. Similar results are obtained when **1** was treated with an equimolar amount of selenium. The generation of the red selenoxo product **4** was reflected by two doublets at δ 383.8 (P1) and 335.0 (P2) ($^1J_{PP}$ = 593.8 Hz). The larger $^1J(^{31}PSe)$ satellite coupling of 753 Hz was observed for P1 whereas $^2J(^{31}PSe)$ was found to be 121.2 Hz. In the heterocycle **5** (δ 108.8 (d), $^1J_{PP}$ = 246.3 Hz)) phosphorus selenium couplings of 111.6 and 131.6 Hz, respectively, were registered. In benzene solution **4** completely rearranged to heterocycle **5** within 2 h at 20 °C. The high propensity for ring formation thwarted the preparation of pure **4**.



From the position of the ^{13}CO signals of the carbonyl ligands in **2** (δ_C 212.9) and **1** (δ_C 216.27) it is clear that the phosphinidene(thioxo)phosphoranyl group is a better acceptor ligand than the diphosphenyl ligand in **1**.[6] This evidence is supported by two strong infrared adsorptions of the $Fe(CO)_2$ moiety in **2** at 2028 and 1980 cm^{-1} (in cyclopentane) (**1**, ν(CO) 2005, 1956 cm^{-1} in cyclopentane). The ^{13}C NMR and infrared data suggest that the σ-donor/π-acceptor properties of the cyclic ligand in **3** is comparable with the P=P—Ar group in **1**.

An X-ray single diffraction determination of **2** was performed, and the results are shown in Figure 1 and Table I.[7] The P=P distance in **2** (2.041 (1) Å) is only slightly elongated as compared to that in **1**. The trigonal-planar phosphorus atom P1 is linked to the chalcogen via a double bond (1.936 (2) Å). These distances as well as the angle P1–P2–C3 (104.8 (1)°) are comparable to distances in the diphosphene monosulfide $t\text{-}Bu_3C_6H_2P({=}S){=}PC_6H_2\text{-}t\text{-}Bu_3$.[4a,8] The iron–phosphorus distance (2.227 (1) Å) is shorter than in that in (2.260 (1) Å) and may be compared with the one in $(2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2P_2Fe(CO)_4$ (2.215 (1) Å).[9,10]

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[5] Experimental details are as follows. **2**. All reactions were carried out in Schlenk tubes under N_2. To a solution of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}PAr$ (**1**) (1.48 g, 2.67 mmol) in 20 mL of THF solid sulfur (0.08 g, 2.50 mmol) was added at 20 °C. After 2 h of stirring and subsequent evaporation of the solvent the dark red residue was crystallized from pentane at 0 °C to give 1.01 g (66%) of dark red crystalline **2** (mp 92 °C): IR (cyclopentane) 2028 (vs), 1980 (vs) cm^{-1} [ν(CO)]; ^1H NMR (C_6D_6) δ 1.37 (s, *p*-*t*-Bu), 1.41 (d, J_{PH} = 1 Hz, C_5Me_5), 1.85 (s, *o*-*t*-Bu), 7.69 (s, *m*-H-aryl); $^{13}C\{^1H\}$ NMR (C_6D_6) δ9.37 (s, $C_5(CH_3)_5$, 31.57 (s, *p*-$C(CH_3)_3$), 33.13 (s) and 33.22 (s, *o*-$C(CH_3)_3$), 35.15 (s, *p*-$C(CH_3)_3$), 38.55 (s, *o* -$C(CH_3)_3$), 98.03 (s, $C_5(CH_3)_5$), 122.43 (d, J_{PC} = 3.9 Hz), 126.61 (d, J_{PC} = 5.6 Hz), 149.81 (d, J_{PC} = 4.6 Hz), 152.52 (d, J_{PC} = 10.3 Hz, C-aryl), 212.94 ("t", J_{PC} = 9.6 Hz, $Fe(CO)_2$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 295.0 (d, $^1J_{PP}$ = 618.5 Hz, P2), 398.0 (d, $^1J_{PP}$ = 618.5 Hz, P1); MS/CI, *m/e* (relative intensity) 589 (M^+ + 3H, 100). Anal. Calcd for $C_{30}H_{44}FeO_2P_2S$: C, 61.43; H, 7.56; Fe, 9.52. Found: C, 62.06; H, 6.02; Fe, 9.54. **3**. Heating a benzene solution of **2** for 2 h under reflux leads to the formation of yellow **3**, which is isolated and purified by column chromatography on Florisil (benzene/hexane, 1:1): yield 60% (mp 139–141 °C); IR (cyclopentane) 2009 (vs), 1953 (vs) cm^{-1} [ν(CO)]; ^1H NMR (C_6D_6) δ 1.18 (s, *p*-*t*-Bu), 1.35 (s, C_5Me_5), 1.87 (s, *o*-*t*-Bu); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 9.06 (d, J_{PC} = 5.5 Hz, $C_5(CH_3)_5$), 31.31 (s, *p*-$C(CH_3)_3$), 34.77 (s) and 34.83 (s, *o*-$C(CH_3)_3$), 34.97 (s, *p*-$C(CH_3)_3$), 39.67 (s) and 39.73 (s, *o*-$C(CH_3)_3$), 96.70 (s, $C_5(CH_3)_5$), 122.67 (s), 139.17 (d, J_{PC} = 2.7 Hz), 141.01 (d, J_{PC} = 3.4 Hz) and 148.31 (s, C-aryl), 156.91 (m, C_{ipso} aryl), 215.26 (dd, J_{PC} = 10.1, 3.1 Hz, Fe(CO)), 216.31 (d, J_{PC} = 8.7 Hz, Fe(CO)); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 83.94 (d, $^1J_{PP}$ = 232.6 Hz, P1), −90.34 (d, $^1J_{PP}$ = 232.6 Hz, P2); MS/EI, *m/e* (relative intensity) 585 (M^+ − H, 3). Anal. Calcd for $C_{30}H_{44}FeO_2P_2S$: C, 61.43; H, 7.56; Fe, 9.52; S, 5.47. Found: C, 61.43; H, 7.52; Fe, 9.47; S, 5.51. **4** and **5**. Analogously compound **1** was combined with an equimolar amount of gray selenium for 2 days. Evaporation to dryness and crystallization of the residue from pentane afforded green-yellow **5** (35%) (mp 123 °C dec). From the red mother liquor impure **4** was isolated as dark red crystals. **4**: IR (cyclopentane) 2029 (st), 1979 (st) cm^{-1} [ν(CO)]; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 334.97 (d, $^1J_{PP}$ = 593.8 Hz, $^2J_{PSe}$ = 121.2 Hz, P2), 383.83 (d, $^1J_{PP}$ = 593.8 Hz, $^1J_{PSe}$ = 753 Hz, P1); MS/CI, *m/e* (relative intensity) 633 (M^+, 100). **5**: IR (cyclopentane) 2003 (s), 1952 (s) cm^{-1} [ν(CO)]; ^1H NMR (C_6D_6) δ 1.18 (s, *p*-*t*-Bu), 1.37 (s, C_5Me_5), 1.85 (s) and 1.86 (s, *o*-*t*-Bu), 7.27 (s) and 7.30 (s, *m*-H-aryl); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 9.06 (s, $C_5(CH_3)_5$), 31.30 (s, *p*-$C(CH_3)_3$), 34.39 (s, *p*-$C(CH_3)_3$), 34.99 (d, J_{PC} = 3.2 Hz, *o*-$C(CH_3)_3$), 35.18 (d, J_{PC} = 3.2 Hz, *o*-$C(CH_3)_3$), 39.68 (s, *o*-$C(CH_3)_3$), 39.75 (s, *o*-$C(CH_3)_3$), 96.79 (s, $C_5(CH_3)_5$), 122.51 (s), 138.22 (d, J_{PC} = 4.5 Hz), 140.08 (d, J_{PC} = 4.0 Hz), 148.30 (s), 157.15 (d, J_{PC} = 3.9 Hz), 157.25 (s, C-aryl), 215.10 (m, Fe(CO)), 216.42 (d, J_{PC} = 8.1 Hz, Fe(CO)); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −66.40 (d, $^1J_{PP}$ = 246.3 Hz, $^1J_{PSe}$ = 131.6 Hz, P2), 108.80 (d, $^1J_{PP}$ = 246.3 Hz, $^1J_{PSe}$ = 111.6 Hz, P1); MS/CI, *m/e* (relative intensity) 633 (M^+, 100). Anal. Calcd for $C_{30}H_{44}FeO_2P_2Se$: C, 56.88; H, 7.00; Fe, 8.82; Se, 12.47. Found: C, 56.79; H, 6.96; Fe, 8.93; Se, 12.39.

[6] (a) Braterman, P. S.; Milne, D. W.; Randall, E.; Rosenberg, E. *J. Chem. Soc., Dalton Trans.* **1973**, 1027. (b) Cotton, F. A.; Hunter, D. L.; Lahuerta, P. *J. Am. Chem. Soc.* **1974**, *96*, 7926.

[7] Crystal data for complex **2**: space group $P\bar{1}$, a = 9.100 (2) Å, b = 13.808 (2) Å, c = 13.890 (3) Å, α = 103.14 (2)°, β = 102.89 (2)°, γ = 97.57 (2)°, V = 1625.8 (6) Å^3, Z = 2, d(calcd) = 1.193 g/cm^3; μ(Mo $K\alpha$) (graphite monochromator) = 6.4 cm^{-1}; $2\theta/\omega$ scan data collection at room temperature ($3° \le 2\theta \le 55°$); 9497 unique reflections, 5601 unique observed ($F_o \ge 4.5\sigma(F)$); Nicolet R3 four-circle diffractometer; structure solving by Patterson and Fourier techniques and refinement by block-cascade least squares using SHELXTL on a Nova 3 (Data General). All non-hydrogen atoms were refined anisotropically with 346 parameters and rigid groups for cyclopentadienyl rings, and all hydrogen atoms were given the 1.2-fold isotropic temperature factor of the U_{ij} tensor of the corresponding C atom: R = 0.067, R_w = 0.070, $w^{-1} = \sigma^2(F) + 0.0079F^2$, and maximum residual electron density = 1.1 e/Å^3.

[8] Average P=S double-bond distances are 1.92 + 0.05 Å: Corbridge, D. E. C. *Phosphorus*, 2nd ed.; Elsevier: Amsterdam, 1980; p27.

[9] Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulsky, M.; Ando, F.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 7751.

Registry No. 1, 98088-31-4; 2, 109744-92-5; 3, 109744-93-6; 4, 109744-94-7; 5, 109744-95-8.

Supplementary Material Available: Tables of fractional coordinates, bond distances, bond angles, anistropic thermal parameters, and hydrogen atom coordinates and isotropic thermal parameters (5 pages); a listing of structure factor amplitudes (56 pages). Ordering information is given on any current masthead page.

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(10) Fe–P bond distances in low-valent carbonyliron complexes usually fall in the range of 2.17–2.35 Å. See, e.g.: (a) Knoll, K.; Huttner, G.; Wasiucionek, M.; Zsolnai, L. *Angew. Chem.* **1984,** *96,* 708; *Angew. Chem., Int. Ed. Engl.* **1984,** *23,* 739. (b) Lal De, R.; Vahrenkamp, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986,** *B41,* 273. (c) Arif, A. M.; Cowley, A. H.; Pakulsky, M. *J. Am. Chem. Soc.* **1985,** *107,* 2553. (d) Huttner, G.; Mohr, G.; Friedrich, G.; Schmid, H. G. *J. Organomet. Chem.* **1978,** *160,* 59. (e) Williams, G. D.; Geoffroy, G. L.; Whittle, R. R.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985,** *107,* 729.

Competitive H–O and H–C Bond Activation in the Reaction of CH_3OH with $(OC)_3Mn^-$

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Summary: The activation of the H–O and H–C bonds in CH_3OH are shown to be competitive in the reaction with $(OC)_3Mn^-$ by product studies and kinetic deuterium isotope effects.

Three oxidative addition pathways involving the H–C,[1] H–O,[2,3] and C–O bonds[3] have been suggested for the reactions of coordinatively unsaturated transition-metal complexes with alcohols. We wish to report the results of product studies and kinetic deuterium isotope effects for the reaction of the 14-electron complex $(OC)_3Mn^-$ with CH_3OH which support intermolecular H–C and H–O oxidative addition as the two competitive channels.

Our gas-phase studies are carried out in a previously described flowing afterglow (FA) apparatus in a fast flow of helium buffer gas (P_{He} = 0.7 torr, $\bar{v}$ = 57 m s^{-1}, 298 K).[4] A mixture containing major signals of $(OC)_3Mn^-$ (*m/z* 139) and $(OC)_4Mn^-$ (*m/z* 167) and a small signal of $(OC)_5Mn^-$ (*m/z* 195) is produced by dissociative electron attachment of energetic electrons with $Mn_2(CO)_{10}$.[5] Neither $(OC)_4Mn^-$ or $(OC)_5Mn^-$ react with CH_3OH, H_2O, or alkanes.

Addition of gaseous CH_3OH to the fast helium flow containing $(OC)_3Mn^-$ produced a fast decay of the signal for $(OC)_3Mn^-$ (*m/z* 139) and generated two product ions at *m/z* 143 and 169 (Table I and eq 1). The ion at *m/z* 143 is the (adduct – CO)$^-$ analogous to the product formed by the oxidative addition of H_2O to $(OC)_3Mn^-$.[5,6] Although $(OC)_2Mn(H)(OH)^-$ [5] undergoes *one* H/D exchange when allowed to react with D_2O,[7] *no* H/D exchange was observed between the *m/z* 143 ion and D_2O or CH_3OD, indicating the absence of the HO ligand. The *m/z* 143 ion reacted with SO_2 to yield $(O_2S)Mn(H)(OCH_3)^-$ (*m/z* 151) by loss of both CO ligands which implies multiple Mn-to-O bonding in *m/z* 143 with the CH_3O ligand serving as a multielectron donor.[5] The product ion at *m/z* 169 (eq 1b) is the (adduct – H_2)$^-$ analogous to the olefin product ions generated by dehydrogenation of alkanes by $(OC)_3Mn^-$.[8] Reaction of the *m/z* 169 ion with SO_2 yields $(OC)_3Mn(SO_2)^-$ (*m/z* 203) with exclusive loss of H_2CO suggesting that H_2O is η^2-bound in the ion at *m/z* 169.[6]

$$\underset{m/z\ 139}{(OC)_3Mn^-} + CH_3OH \xrightarrow{0.29} \underset{m/z\ 143}{(OC)_2Mn(H)(OCH_3)^-} + CO \tag{1a}$$

$$\underset{m/z\ 139}{(OC)_3Mn^-} + CH_3OH \xrightarrow{0.71} \underset{m/z\ 169}{(OC)_3Mn(H_2CO)^-} + H_2 \tag{1b}$$

The reactions of $(OC)_3Mn^-$ with various deuteriated methanol molecules were examined to determine the source of H_2 in the major product channel 1b and the kinetic deuterium isotope effects on both product forming channels. The elimination of HD in the reactions of $(OC)_3Mn^-$ with CH_3OD and CD_3OH yielding $(OD)_3Mn(H_2CO)^-$ (*m/z* 169) and $(OC)_3Mn(D_2CO)^-$ (*m/z* 171), respectively, establish the origin of H_2 in channel 1b as the H–O bond and a H–C bond in the CH_3OH molecule (Table I).

The kinetic and product data for the reactions of $(OC)_3Mn^-$ with CH_3OH, CH_3OD, CD_3OH, and CD_3OD are given in Table I. Although the errors in the reproducibility of the rate constants and product channel branching fractions are significant, we have calculated the rate constants for the separate product forming channels by using the average k_{total} and average branching fractions. The good agreement in the two values each obtained for k_{CH_3} and k_{CD_3} in these experiments strongly suggests that the initial intermolcular oxidative addition of the H–C and D–C to $(OC)_3Mn^-$ is rate limiting in channel 1b and that the intramolecular migration of H or D from oxygen to the metal is fast and does not contribute to the rate. A similar conclusion was reached for the inter- and intramolecular steps in the related dehydrogenation of alkanes by $(OC)_3Mn^-$.[8] With use of the average of the two values for k_{CH_3} and k_{CD_3}, $k_{CH_3}/k_{CD_3} \approx 2.4$.

The rate constant k_{OD} derived in the reactions of $(OC)_3Mn^-$ with CH_3OD and CD_3OD will have the larger error since these channels involve the smallest product ion signal intensities. However, the good agreement in the two results in Table I support $k_{OD} \approx 4.8 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} in these reactions. Thus, $k_{OH}/k_{OD} \approx 7$ is calculated for channel 1a involving oxidative addition of the H–O bond

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(1) *Chem. Eng. News* **1985,** 53 describes the paper of Professor R. G. Bergman given at the PAC CHEM 1984 meeting, and private communications with Professor Bergman. Products of exclusive H–C oxidative addition were observed or inferred by J. C. Hayes and P. O. Stoutland when mixtures of $[c\text{-}C_5(CH_3)_5][(CH_3)_3P]Ir(H)_2$ in *tert*-butyl alcohol or ethanol were irradiated in the condensed phase.

(2) Lane, K. R.; Squires, R. R. *J. Am. Chem. Soc.* **1985,** *107,* 6403.

(3) McElvany, S. W.; Allison, J. *Organometallics* **1968,** *5,* 416, 1219.

(4) (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985,** *107,* 4123. (b) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *Ibid.* **1980,** *102,* 6491.

(5) McDonald, R. N.; Chowdhury, A. K.; Jones, M. T. *J. Am. Chem. Soc.* **1986,** *108,* 3105.

(6) The reverse of the present oxidative addition reactions involving selective reductive elimination of CH_3OH from $(Me_3P)_2(Cl)(OC)Rh(H)(OCH_3)$ and of H_2CO from $(Me_3P)_2(Cl)(OC)Rh(H)(CH_2OH)$ was recently proposed: Milstein, D. *J. Am. Chem. Soc.* **1986,** *108,* 3525.

(7) We believe that the *fast, single* H/D exchange observed in the reaction of $(OC)_2Mn(H)(OH)^-$ with D_2O occurs on the HO ligand via a four-centered intermediate or transition state. If $(OC)_2Mn(H)(OH)^-$ had oxidatively added D_2O, the possible products could be the starting complex ion containing one and two deuteriums (*m/z* 144 and 145) formed by retroaddition along with the HD elimination product $(OC)_2Mn(OH)(OD)^-$; $(OC)Fe(H)(OH)^{\bullet-}$ slowly added H_2O to yield $(OC)Fe(OH)_2^{\bullet-}$.[5] $(OC)_2Mn(H)(OH)^-$ failed to react with H_2O ($k < 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}) under these same reaction conditions.[5]

(8) McDonald, R. N.; Jones, M. T. *J. Am. Chem. Soc.* **1986,** *108,* 8097.

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