ORGANOMETALLICS

Bimetallic .mu.-malonyl compounds. Synthesis, characterization, and reactivity of (.eta.5-C5Me5)Re(NO)(PPh3)-cyclo[(.mu.-.eta.1,.eta.2-COCH2CO)M(CO)4] (M = Re, Mn)

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Organometallics, **1987**, 6 (9), 1987-1989• DOI: 10.1021/om00152a027 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

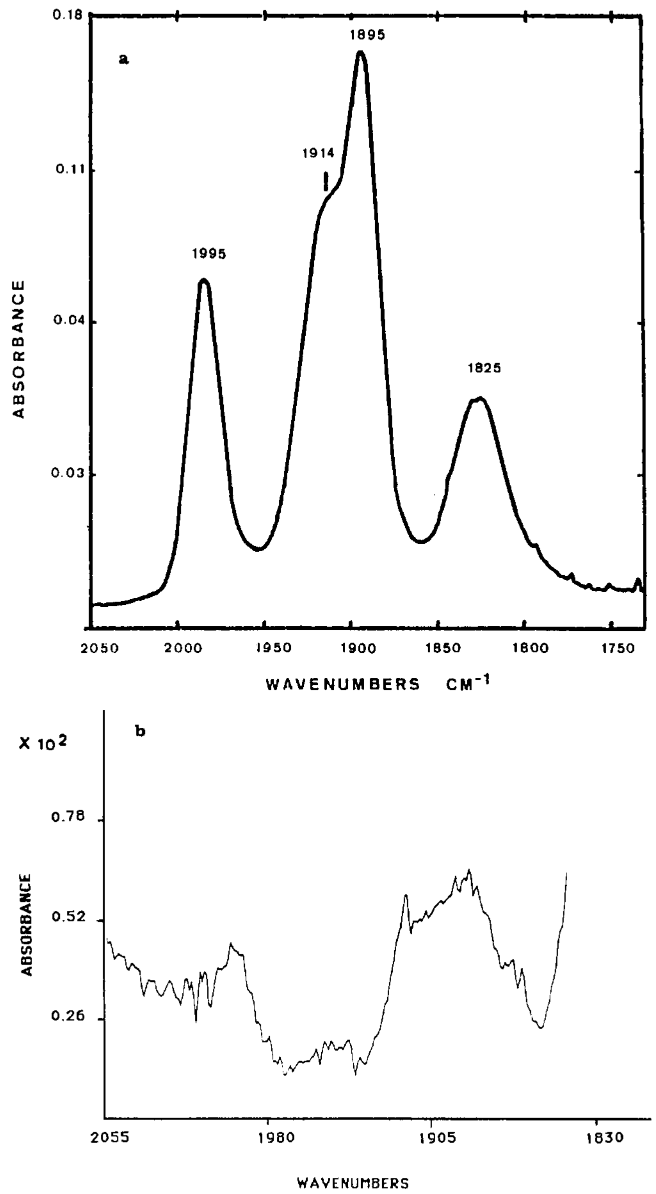

Figure 1. (a) FT-IR spectrum of compound **6** in $CHCl_3$ (30 scans at 2 cm^{-1} resolution). (b) FT-IR difference spectrum ν(CO) region obtained by subtracting the spectrum of precipitated protein, following incubation with compound **6** (1×10^{-8} M) in the presence of diethylstilbestrol (DES, 1×10^{-3} M), from that of precipitated protein incubated with compound **6** (1×10^{-8} M) in the absence of DES.

the choice of IR detector for these extremely low concentration measurements is a critical factor in detecting the ν(CO) peaks of the organometallic carbonyl cluster labels. We were unsuccessful by using the more conventional triglycine sulfate (TGS) and liquid-nitrogen-cooled mercury–cadmium–telluride (MCT) detectors and had to resort to the more sensitive liquid-nitrogen-cooled indium–antimonide (In/Sb) detector. Attempts to detect specific binding of a cobalt cluster labeled steroid through the agency of a doubly labeled species by exchange of some of the CO groups with ^{14}CO (specific activity = 50 mCi/mmol) failed essentially because the level of precision for ^{14}C detection proved to be insufficient.

The use of organometallic carbonyl cluster complexes as IR markers for biological systems augers well for the future since (a) the binding affinities when these types of molecules are attached to hormonal steroids are reasonably comparable to those of the free steroids themselves, (b) the labeled steroids are sufficiently soluble and stable in biological media for long periods of time, and (c) their ν(CO) peaks are strong enough to be detected by commercially available FT-IR spectrometers at about the femtomole concentration levels associated with hormone receptor sites by virtue of the fortuitous IR spectral window available in the case of proteins. Preliminary work on extending the applications of IR markers to other biological areas, e.g., other hormone receptors, mycotoxins, peptides and drugs, has already begun.

Acknowledgment. This research was generously supported by operating and equipment grants from NSERC (Canada), FCAR (Quebec) and CNRS, ANVAR, PIRMED, and Bruker (France) and has benefitted greatly from the France-Quebec Exchange Program. H. Buijs and J. Dykeman (Bomem, Quebec) are especially thanked for recording some of the spectra and for their invaluable technical advice. We also wish to thank M. Pankovski for helpful discussion and A. Cordaville and B. Malezieux for technical assistance.

Registry No. **1**, 57-63-6; **2**, 101915-79-1; **3**, 93122-00-0; **4**, 109282-00-0; **5**, 109282-01-1; **6**, 109306-28-7; e, 50-28-2.

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[17] The specific-bound fractions were determined in parallel experiments by incubation of lamb uterine cytosol at 0 °C for 3 h with [6,7-^{3}H]-17β-estradiol (2×10^{-9} M; specific activity = 52 Ci/mmol).

Bimetallic μ-Malonyl Compounds. Synthesis, Characterization, and Reactivity of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}\overline{COCH_2CO)M}(CO)_4$ (M = Re, Mn)

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Summary: Rhenaenolate, $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(COCH_2Li)$, generated in situ from $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(COCH_3)$ and *n*-BuLi, reacts with $M(CO)_5(OSO_2CF_3)$ (M = Re, Mn) to give the first μ-malonyl complexes $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}\overline{COCH_2CO)M}(CO)_4$ (**1-Re**, M = Re; **1-Mn**, M = Mn). The enolate anion of **1-Re** undergoes both diastereoselective alkylation and regioselective silylation chemistry to give **3** and **4**, respectively.

The role of acyl species in metal-catalyzed CO chemistry has for many years focused attention on the synthesis and properties of transition-metal acyl complexes. In view of the central place that carbonyl compounds claim in organic chemistry, a significant recent development is the increased utilization of acyl complexes for organic synthesis. A number of groups have now employed transition-metal enolate anions, derived by deprotonation of acyl complexes, as reagents for stereoselective carbon–carbon bond formation.[1] In contrast to simple metal acyl species, tran-

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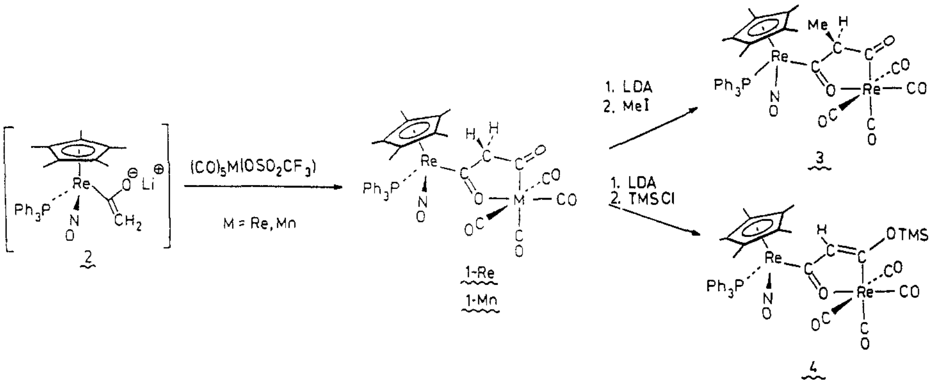
Scheme I



sition-metal derivatives of the 1,3-dicarbonyl moiety are rare and their chemistry is largely unexplored. Here we report the synthesis, characterization, and reactivity of the first homo- and heterobimetallic μ-malonyl compounds **1-Re** and **1-Mn**.[2] Malonyl-bridged bimetallic complexes, such as **1-Re** and **1-Mn**, have potential for modification of acyl reactivity patterns and serve as intriguing model compounds for possible surface-bound intermediates in metal-catalyzed carbon monoxide chemistry.[3]

Reaction of $(CO)_5Re(OSO_2CF_3)$ and 1 equiv of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(COCH_2Li)$[4] (**2**), generated in situ from $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(COCH_3)$ and *n*-BuLi at −78 °C, gives the μ-malonyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}COCH_2CO)Re(CO_4)$ (**1-Re**) as an air-stable yellow solid (71%).[5] The heterobimetallic μ-malonyl complex **1-Mn** was prepared in a similar manner, also as an air-stable yellow solid (52% yield).[5]

The ^1H NMR spectrum of **1-Re** in chloroform-d_1 includes an AB pattern due to diastereotopic methylene protons (δ 2.48 (d, J = 20.7 Hz, 1 H) and 3.13 (d, J = 20.7 Hz, 1 H)). In the $^{13}C\{^1H\}$NMR spectrum a doublet at δ 289.8 (J_{CP} = 7.4 Hz) and a singlet at δ 275.6 are assigned to the malonyl carbonyl carbons. The mutually trans, terminal carbonyl ligands are also diastereotopic owing to the stereogenic rhenium center, and four distinct carbon resonances are observed at δ 190.9, 191.4, 191.6, and 194.9.

To confirm the presence of a μ-η^1,η^2-malonyl bridge and to characterize structurally this new class of materials, an X-ray diffraction study was performed on **1-Mn**. (Figure 1).[6] The rhenium-malonyl–manganese fragment in **1-Mn** deviates from perfect planarity with maximum deviations from the ReCOCCOMn plane at C(12), 0.097 Å, and at C(13), −0.098 Å. In related rhenium acyl compounds, extended Hückel MO calculations indicate that the ON–Re–C_α-O torsion angle (θ) should be near 0° or 180°.[7] For **1-Mn**, θ is 177.6°, which places the C(11)–O(2) oxygen anti to the NO ligand. Both the Re–C(11) distance of 2.046 Å and the Mn–C(13) distance of 2.024 Å are closer to corresponding metal–carbon double-bond distances than to metal–carbon single-bond distances.[8] This, together with

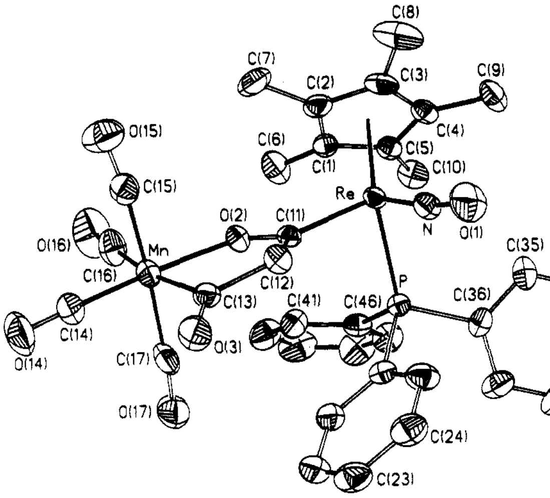


Figure 1. Molecular structure and labeling scheme for **1-Mn**. Bond distances (Å) and angles (deg): CNT–Re, 1.984 (5); Re–P, 2.384 (1); Re–N, 1.757 (4); Re–C(11), 2.046 (4); Mn–O(2), 2.050 (3); Mn–C(13), 2.024 (5); O(2)–C(11), 1.272 (5); C(11)–C(12), 1.506 (7); C(12)–C(13), 1.526 (6); C(13)–O(3), 1.211 (7); CNT–Re–P, 127.9 (1); CNT–Re–N, 124.9 (2); CNT–Re–C(11), 117.6 (2); P–Re–N, 91.9 (1); P–Re–C(11), 87.2 (1); N–Re–C(11), 98.0 (2); Re–C(11)–O(2), 122.9 (3); Re–C(11)–C(12), 123.5 (3); O(2)–C(11)–C(12), 113.3 (3); C(11)–C(12)–C(13), 112.7 (4); C(12–C(13)–O(3), 118.1 (4); Mn–C(13)–O(3), 130.8 (3); Mn–O(2)–C(11), 120.7 (3); O(2)–Mn–C(13), 80.1 (2).

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[1] (a) Theopold, K. H.; Becker, P. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 5250. (b) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733. (c) Brinkman, K.; Helquist, P. *Tetrahedron Lett.* **1985**, *26*, 2845. (d) Davies, S. G.; Walker, J. C. *J. Chem. Soc., Chem. Commun.* **1985**, 209 and references therein. (e) Ojima, I.; Kwon, H. B. *Chem. Lett.* **1985**, 1327. (f) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328 and references therein. (g) Rusik, C. A.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 4652.

[2] Seppelt recently reported the synthesis of an η^1,η^1-difluoromalonyl homodinuclear complex, $[Mn(CO)_5]_2(\mu\text{-}\eta^1,\eta^1\text{-}COCF_2CO)$, from reaction of $Na[Mn(CO)_5]$ and $ClCOCF_2COCl$: Schulze, W.; Hartl, H.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 185.

[3] (a) Formally, μ-malonyl complexes result from carbon monoxide insertion into both metal–carbon bonds of surface-bound methylene species. Insertion of carbon monoxide into the carbon–metal bond of a μ-methylene complex has been observed: Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679. Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 254. (b) Diethyl malonate is a major product of the Pd/Al_2O_3-catalyzed reaction of CO, ketene, and ethyl nitrite: Ube Industries, Ltd., Eur. Pat. Appl. 6611 (Cl. CO7C69138), 1980 (*Chem. Abstr.* **1980**, *93*, 45987).

[4] Heah, P. C.; Patton, A. T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1185.

[5] Complexes **1-Re**, **1-Mn**, **3**, and **4** have been characterized by ^1H NMR, ^{13}C NMR, IR, mass spectroscopy, and microanalysis. Details are provided as supplementary material.

[6] Suitable crystals of **1-Mn** were grown by slow evaporation of a CH_2Cl_2 solution. A yellow specimen (0.26 × 0.30 × 0.36 mm) belonged to the triclinic space group $P\bar{1}$: a = 10.533 (2) Å, b = 10.920 (2) Å, c = 16.595 (5) Å, α = 74.58 (2)°, β = 83.48 (3)°, γ = 68.49 (2)°; V = 1711.5 (9) Å^3; Z = 2, D(calcd) = 1.65 g cm^{-3}; μ(Mo Kα) = 42.2 cm^{-1}; T = 293 K. Of 6974 absorption corrected data collected (Nicolet + R3m, $4° \leqslant 2\theta \leqslant 52°$), 6731 were independent (R_{int} = 1.67%), and 5809 were observed at the 3σ level. With all non-hydrogen atoms anisotropic and found hydrogen atoms isotropic: $R(F)$ = 2.81, $R(wF)$ = 2.99 [$R(F)$ all data = 3.57], $\Delta(\rho)$ = 1.32 e Å^{-3} (0.94 Å Re), and N_o/N_v = 13.2.

[7] Bodner, G. S.; Patton, A. T.; Smith, D. E.; Georgiou, S.; Tam, W.; Strouse, C. E.; Gladysz, J. A., submitted for publication in *Organometallics*.

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] $Mn({=}CO(CH_3)(OEt))(CO)_4(CH_3C_6H_5\text{-}1\text{-}NpGe)$, 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**, $ON\text{-}Re\text{-}C_\alpha\text{-}O$ and $OC\text{-}Fe\text{-}C_\alpha\text{-}O$ 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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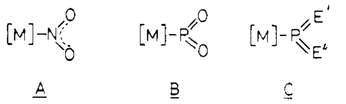
Received April 8, 1987

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.