*Russian Chemical Bulletin, International Edition, Vol. 56, No. 7, pp. 1477—1479, July, 2007* 1477

# Letters to the Editor

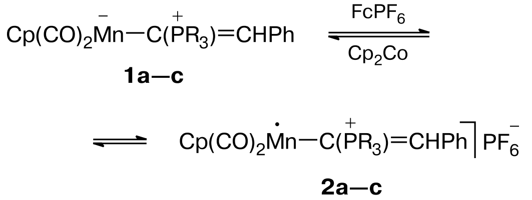
## Stable 17e complexes $[\mathrm{Cp(CO)_2Mn{-}C(PR_3){=}CHPh}]\mathrm{PF_6}$

*V. V. Krivykh,* E. S. Taits, S. P. Solodovnikov, I. V. Glukhov, M. Yu. Antipin, and N. A. Ustynyuk**

*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
*28 ul. Vavilova, 119991 Moscow, Russian Federation.*
*Fax: +7 (495) 135 5085. E-mail: vkriv@ineos.ac.ru, ustynyuk@ineos.ac.ru*

Only a few stable carbonyl-containing open-shell transition metal complexes are known. The stability of 17-electron (17e) complexes can be increased by either introducing bulky substituents into the ligands or replacing CO ligands with electron-donating tertiary phosphines, S- or Se-containing ligands.[1]

We found the first example of stabilization of 17e complexes, in which the phosphorus atom is present in an organic ligand rather than is directly bound to the metal atom. Stable phosphoniostyryl 17e complexes **2a—c** were prepared by oxidation of, respectively, zwitterionic adducts **1a,b** [2] and adduct **1c**, which was synthesized analogously (Scheme 1).



$$\mathrm{Cp(CO)_2\overset{-}{Mn}{-}C(\overset{+}{P}R_3){=}CHPh}\ \underset{\mathrm{Cp_2Co}}{\overset{\mathrm{FcPF_6}}{\rightleftharpoons}}\ \left[\mathrm{Cp(CO)_2\overset{\bullet}{Mn}{-}C(\overset{+}{P}R_3){=}CHPh}\right]\mathrm{\overset{-}{PF_6}}$$

**1a—c** **2a—c**

$R_3$ = $Ph_3$ (**a**), $Ph_2Me$ (**b**), $PhMe_2$ (**c**)

The stability of complexes **2a—c** is comparable to that of structurally similar 18e manganese derivatives, for example, of the vinylidene complex $\mathrm{Cp(CO)_2Mn{=}C{=}CHPh}$. In the solid state, complexes **2a—c** are stable at –(10–15) °C for a long period of time; in a dichloromethane solution for several hours. The reaction of reducing agents (cobaltocene or sodium amalgam) with complex **2** resulted in regeneration of adduct **1**. The structures of the reaction products were determined by elemental analysis, IR spectroscopy, and ESR spectroscopy. The structure of complex **2b** was established by X-ray diffraction.

The ESR parameters of complexes **2a—c** are similar to those of the $[\mathrm{Cp(CO)_2MnPR_3}]^+$ (**3**) and $[\mathrm{Cp(CO)Mn(PR_3)_2}]^+$ complexes (**4**) (R = Ar or Alk),[3] which is evidence in favor of the low-spin nature of **2a—c**. The isotropic character of the hyperfine coupling constants is indicative of the partial spin density delocalization to the phosphorus atom through the carbon atom. It should be noted that the two-bond coupling constants $a_\mathrm{P}(^{31}\mathrm{P})$ are twice as small as those for complexes **3** and **4** and are equal to 1.5 mT.

The Mn—[C(6)—C(10)], Mn—C(11), and C(11)—C(12) bond lengths in complex **2b** determined by X-ray diffraction are similar to those in the $\mathrm{Cp(CO)_2Mn{-}C(PPh_3){=}C{=}CPh_2}$ complex (**5**).[2] To the contrary, the Mn—CO bonds in **2b** are ~0.05 Å longer than those in complex **5** (Fig. 1). The most substantial

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1423—1424, July, 2007.

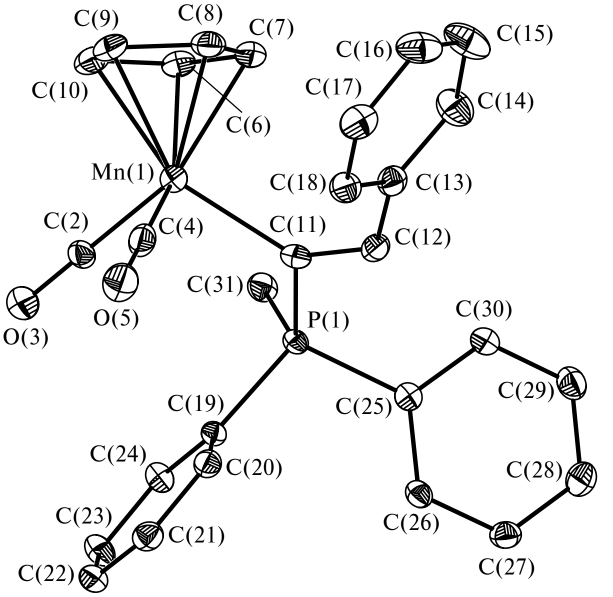


**Fig. 1.** Molecular structure of **2b**. Selected geometric parameters: Mn(1)—C(2), 1.814(5) Å; Mn(1)—C(4), 1.799(6) Å; Mn(1)—C(6), 2.135(5) Å; Mn(1)—C(7), 2.124(5) Å; Mn(1)—C(8), 2.128(5) Å; Mn(1)—C(9), 2.161(5) Å; Mn(1)—C(10), 2.168(5) Å; Mn(1)—C(11), 2.060(5) Å; C(11)—C(12) 1.328(6) Å; C(2)—Mn(1)—C(4), 81.0(2)°. The displacement ellipsoids are drawn at the 30% probability level.

difference between **2b** and **5** is that the OC—Mn—CO angle in the former complex is ~10° smaller, which is apparently characteristic of the 17e $CpM(CO)_2L$-type complexes. This fact has been demonstrated earlier[4] by X-ray diffraction and theoretical calculations for the 18e complex $Cp^*(CO)_2MnPMe_3$ and the 17e complex $Cp^*(CO)_2CrPMe_3$.

All operations associated with the synthesis and isolation of the complexes were carried out under argon with the use of water-free solvents. The IR spectra were recorded in the 1800—2100 $cm^{-1}$ region on a Specord 75 IR spectrophotometer in $CH_2Cl_2$. The ESR spectra were measured on a Varian E-12 spectrometer equipped with a double resonator. One resonator contained the sample under study, another one the reference compound. The elemental analysis was carried out on a VRA-30 X-ray fluorescence spectrometer (Karl Zeiss, Jena).

**Dicarbonyl(β-methyldiphenylphosphoniostyryl)(η$^5$-cyclopentadienyl)manganese(II) hexafluorophosphate (2b).** Ferrocenium hexafluorophosphate (132 mg, 0.4 mmol) and adduct **1b** (192 mg, 0.4 mmol) were added with stirring to dichloromethane (3 mL) cooled to −78 °C. The cooling bath was removed, and the reaction mixture was allowed to warm to 0 °C. Then diethyl ether (12 mL) was added. After 30 min, the precipitate that formed was filtered off, washed with diethyl ether, and dried. Complex **2b** was obtained in a yield of 249 mg (100%), t.decomp. 119 °C. Found (%): C, 53.77; H, 3.86; Mn, 9.00; P, 9.41. $C_{28}H_{24}F_6MnO_2P_2$. Calculated (%): C, 53.95; H, 3.88; Mn, 8.81; P, 9.94. IR, ν/$cm^{-1}$: 2017, 1929 (CO).

**Dicarbonyl(β-triphenylphosphoniostyryl)(η$^5$-cyclopentadienyl)manganese(II) hexafluorophosphate (2a)** was synthesized analogously to compound **2b**. The yield was 95%, t.decomp. 117 °C. Found (%): C, 55.13; H, 3.70; P, 8.41. $C_{33}H_{26}F_6MnO_2P_2 \cdot 0.5\ CH_2Cl_2$. Calculated (%): C, 55.27; H, 3.74; P, 8.51. IR, ν/$cm^{-1}$: 2019, 1929 (CO). ESR (20 °C, $CH_2Cl_2$—$C_2H_4Cl_2$ (1 : 1)): $g_{iso} = 2.0635$, $a_{Mn} = 5.5$ mT. Hyperfine coupling $a_P = 1.5$ mT was observed only on high-field components. At 77 K, the anisotropy of the *g* factor and the hyperfine coupling constant with the manganese nucleus was observed ($g_1 = 2.1280$, $a_{1Mn} = 11$ mT; $g_2 = 2.0971$, $a_{2Mn} = 0.5$ mT; $g_3 = 1.9654$, $a_{3Mn} = 5$ mT), while the anisotropy for the phosphorus nucleus was absent.

**Dicarbonyl(β-dimethylphenylphosphoniostyryl)(η$^5$-cyclopentadienyl)manganese(II) hexafluorophosphate (2c)** was synthesized analogously to compound **2b**. The yield of 92%, t.decomp. 120 °C. Found (%): C, 49.27; H, 3.94; Mn, 10.30; P, 11.01. $C_{23}H_{22}F_6MnO_2P_2$. Calculated (%): C, 49.22; H, 3.95; Mn, 9.77; P, 11.01. IR, ν/$cm^{-1}$: 2020, 1929 (CO).

**Reduction of complexes 2b.** Tetrahydrofuran (2 mL) and complex **2b** (63 mg, 0.1 mmol) were added to sodium amalgam, which was prepared from Na (5 mg) and mercury (0.5g). The reaction mixture was magnetically stirred for 20 min and then chromatographed on a silica gel column at −40 °C using dichloromethane as the eluent. Compound **1b** was isolated in a yield of 31 mg (65%) from the orange band, which was concentrated and triturated with hexane. IR, ν/$cm^{-1}$: 1898, 1829 (CO).

**X-ray diffraction study.** Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a solution of **2b** in dichloromethane. $C_{28.5}H_{25}ClF_6MnO_2P_2$, $M = 665.82$, triclinic crystals, space group $P\bar{1}$, at $T = 100$ K, $a = 10.2620(13)$ Å, $b = 10.6293(14)$ Å, $c = 14.5861(17)$ Å, $\alpha = 81.362(2)°$, $\beta = 73.730(3)°$, $\gamma = 84.837(3)°$, $V = 1508.1(3)$ Å$^3$; $F(000) = 676$, $d_{calc} = 1.466$ g $cm^{-3}$, $\mu = 0.694$ $mm^{-1}$. The unit cell parameters and the intensities of 10814 reflections were measured on an automated Bruker Apex2 diffractometer ($T = 100$ K, λMo-Kα radiation, graphite monochromator, φ- and ω-scanning technique, $\theta_{max} = 26°$). The absorption correction was applied using the SADABS program.[5] The structure was solved by direct methods and refined by the full-matrix least-squares technique with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms were placed geometrically and refined isotropically with fixed positional (riding model) and thermal parameters. The final *R* factors were $R_1 = 0.0606$ for 4012 independent reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1429$ for all 5840 independent reflections. All calculations were carried out with the use of the SHELXTL PLUS program package (Version 5.10).[6]

This study was financially supported by the Russian Foundation for Basic Research (Project No. 05-03-32720) and the Presidium of the Russian Academy of Sciences (Program of Basic Research "Development of Methods for the Synthesis of Chemical Compounds and Design of New Materials").

## References

1. S. Sun and D. A. Sweigart, *Adv. Organomet. Chem.*, 1996, **40**, 171.
2. N. E. Kolobova, L. L. Ivanov, O. S. Zhvanko, O. M. Khitrova, A. S. Batsanov, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1984, **265**, 271.
3. R. D. Pike, A. L. Rieger, and P. H. Rieger, *J. Chem. Soc., Faraday Trans.*, 1989, **85**, 3913.
4. S. Fortier, M. C. Baird, K. F. Preston, J. R. Morton, T. Ziegler, T. J. Jaeger, W. C. Watkins, J. H. MacNeil, K. A. Watson, K. Hensel, Y. Le Page, J.-P, Charland, and A. J. Williams, *J. Am. Chem. Soc.*, 1991, **113**, 542.
5. G. M. Sheldrick, *SADABS, V2.01, Bruker/Siemens Area Detector Absorbtion Correction Program; Bruker AXS Inc.*, Madison, WI, 1998.
6. G. M. Sheldrick, *SHELXTL, V5.10, Bruker AXS Inc.*, Madison, WI, 1998.

*Received January 31, 2007;*
*in revised form April 9, 2007*