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New Complexes of Iron, Manganese and Molybdenum with 2-Diphenylphosphinoethanethiol as 3- and 5-electron Chelating Ligand

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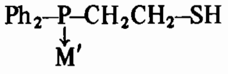
2-Diphenylphosphinoethanethiol (L) is potentially a versatile ligand which *a priori* can yield five types of metal complexes:

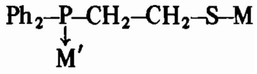
$Ph_2P{-}CH_2{-}CH_2{-}S{-}M$

1e

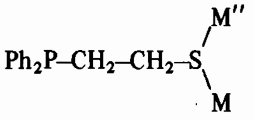
(unlikely with class 'b' transition metals)


$\underset{\displaystyle M'}{\underset{\downarrow}{Ph_2P}}{-}CH_2CH_2{-}SH$

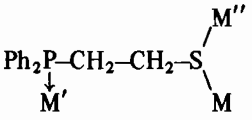
2e


$\underset{\displaystyle M'}{\underset{\downarrow}{Ph_2P}}{-}CH_2{-}CH_2{-}S{-}M$

3e


$Ph_2P{-}CH_2{-}CH_2{-}S{\begin{matrix} / M'' \\ \backslash M \end{matrix}}$

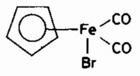
3e


$\underset{\displaystyle M'}{\underset{\downarrow}{Ph_2P}}{-}CH_2{-}CH_2{-}S{\begin{matrix} / M'' \\ \backslash M \end{matrix}}$

5e

In both 3- and 5-electron complexes L can be used either as chelating or as bridging ligand.

However, in spite of its very interesting potential, (L) has been only poorly studied in coordination chemistry. 3-electron anionic chelates have been synthesized with chromium, molybdenum and tungsten carbonyls [1] on the one hand, and on the other, the full structural study of a neutral chelate with Mo^{IV} has appeared very recently [2]. (This last paper prompted us to report on our own results). Besides gold complexes in which (L) acts as a 3-electron bridging ligand have been described [3]. As far as we know, these are the only complexes of (L) which have been fully characterized up to date. As the starting point for a more systematic study of P, S donors in coordination chemistry [4] we have decided to prepare some new neutral complexes of (L) in order to detect new coordination modes of (L) if possible. For that purpose the S-Na derivative of (L) prepared by reacting (L) [5] with NaH in anhydrous THF under Argon was reacted with monobromometal derivatives *1*, *2*, *3*.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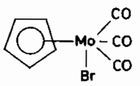
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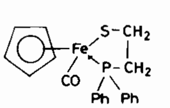
$(OC)_5Mn{-}Br$

3

After filtration of the precipitate (NaBr) and THF evaporation, the crude product was purified by chromatography on neutral alumina.

In the first case, complex *4* was obtained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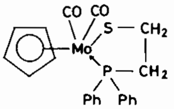
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as a deep red solid in 34% yield (mp ~100 °C; eluted with CH_2Cl_2) and fully characterized: *Anal.* Found C, 59.36; H, 4.92; Fe, 14.10; P, 7.94; S, 7.85; Calc. for $C_{20}H_{19}FeOPS$: C, 60.96; H, 4.86; Fe, 14.21; P, 7.86; S, 8.12; ^1H NMR (in $CDCl_3$, internal TMS); δ, 2.63 (m, 4H, $(CH_2)_2$); 4.40 (d, $^3J_{HP}$ 1 Hz, 5H, Cp); 7.37–7.53 (m, 10H, Ph) ppm; ^{31}P NMR ($CDCl_3$, external 85% H_3PO_4, + for downfield shifts) δ + 67 ppm, IR (CH_2Cl_2) ν_{CO}, 1935 cm^{-1}; mass spectrum (70 eV) m/e: 394 (M, 12%); 366 (M–CO, 44%); 121 (100%). The mass spectrum clearly establishes the monomeric chelated structure. The very high phosphorus shift upon complexation is noteworthy (δ $^{31}P(L) = -18.1$ ppm).

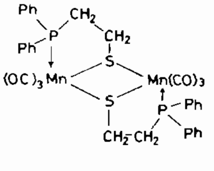
The same type of result was obtained in the case of Molybdenum. Complex *5* was obtained as an orange solid in 20% yield (m.p. ~200 °C, eluted with CH_2Cl_2). *Anal.* Found C, 54.60; H, 4.10; Mo, 20.38; P, 6.80. Calc. for $C_{21}H_{19}MoO_2PS$: C, 54.53; H, 4.14; Mo, 20.76; P, 6.70; ^1H NMR: δ, 2.64 (m, 4H, $(CH_2)_2$); 5.15 (d, $^3J_{HP}$ 0.3 Hz, 5H, Cp); 7.4–7.55 (m, 10H, Ph) ppm; ^{31}P NMR δ + 88 ppm; IR ν_{CO}: 1945, 1865 cm^{-1}.

A complete interpretation of the mass spectrum has been attempted: m/e (^{98}Mo): 464 (M, 17%);

436 (M–CO, 40%); 408 (M–2CO, 27%); 380 (408–C_2H_4, 97%); 303 (380–Ph, 37%); 271 (303–S, 67%); 183 (100%).

The decomposition of (L) in the coordination sphere of Molybdenum is especially interesting. The first step of it is the loss of the $(CH_2)_2$ bridge between phosphorus and sulfur followed by the cleavage of a phosphorus–phenyl bond.

The most interesting result was obtained with *3*. In that case a poorly soluble yellow solid was obtained in 27% yield (m.p. 180–200 °C; eluted with C_6H_6). The elemental analysis did not allow us to discriminate between an $[(L)Mn(CO)_4]_n$ and an $[(L)Mn(CO)_3]_n$ formulation: Found: C, 52.88; H, 3.68; Mn, 13.95; P, 7.80; S, 7.72. Calc. for $C_{18}H_{14}MnO_4PS$: C, 52.43; H, 3.42; Mn, 13.32; P, 7.51; S, 7.78. Calc. for $C_{17}H_{14}MnO_3PS$: C, 53.13; H, 3.67; Mn, 14.30; P, 8.06; S, 8.34. The mass spectrum was useless because it contained only decomposition peaks (the volatility of the product was much too low). However, an approximate molecular weight measurement by comparative tonometry in benzene at 60 °C was obtained in spite of the low solubility. The result ($M = 850 \pm 10\%$) clearly indicated that the product was dimeric. Since we checked that phosphorus was complexed on Manganese by ^{31}P NMR ($\delta^{31}P(C_6D_6) = 26$ ppm), (L) could be either a chelating or a bridging ligand as depicted in formula *6* and *7*.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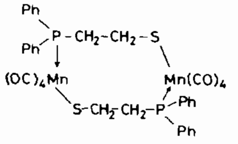
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However the infra-red spectrum left no doubt about the formulation. Various $[RSMn(CO)_4]_2$ complexes have been described in the literature [6]; the $Mn(CO)_4$ group yielded 4 stretching frequencies above or around 2000 cm^{-1}, whereas our compound showed only 3 bands at 1912, 1921, 1995 cm^{-1} in CH_2Cl_2 (1910s, 1930s, 1990s cm^{-1} in KBr). These values were very close to those found by Abel and co-workers [7] for $[Ph_3PMn(CO)_3SR]_2$ complexes for which 3 strong bands have been found between 1900 and 2000 cm^{-1}. Thus the correct formulation of our product is very probably *6* which represents the first example in which (L) plays the role of a 5-electron ligand.

References

1 G. Doyle, *J. Organometal. Chem., 101,* 85 (1975).

2 J. Chatt, J. R. Dilworth and J. A. Schmutz, *J. Chem. Soc. Dalton,* (1979).

3 J. Weinstock, B. M. Sutton, G. Y. Kuo, D. T. Walz and M. J. Di Martino, *J. Med. Chem., 17,* 139 (1974).

4 The very limited work published on this topic has been reviewed: O. Stelzer, 'Transition metal complexes of Phosphorus ligand', in 'Topics in Phosphorus Chemistry', Vol. 9. E. J. Griffith and M. Grayson, Eds, Wiley–Interscience, New York (1977) p. 65.

5 (L) was prepared according to a procedure described in a patent: Fr. 1,401,930, *Chem. Abstracts, 63,* 11615h (1965). See also reference (2).

6 See for example, A. G. Osborne and F. G. A. Stone, *J. Chem. Soc. A,* 1143 (1966).

7 E. W. Abel, A. M. Atkins, B. C. Crosse and G. V. Hutson, *J. Chem. Soc. A,* 687 (1968).