Journal of Organometallic Chemistry, 190 (1980) C25—C27

Preliminary communication

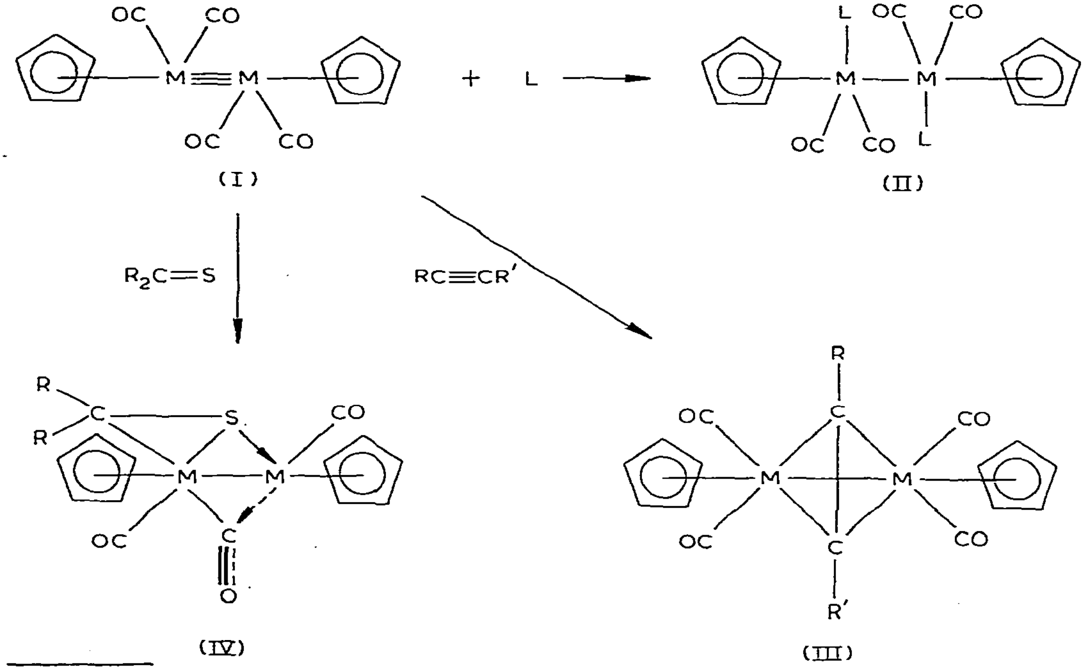
FORMAL 1,1-ADDITION TO A METAL—METAL TRIPLE BOND

HOWARD ALPER*,* and JUDITH HARTGERINK
Department of Chemistry, University of Ottawa, Ottawa, Ontario, K1N 9B4 (Canada)
(Received January 17th, 1980)

Summary

Triphenylphosphine sulfide adds to the triple bond of bis(cyclopentadienyldicarbonyl-molybdenum) (and -tungsten) to give metal—metal single bonded complexes in which two phosphine sulfide ligands are attached to the same metal atom.

Much work has been done in recent years on the chemistry of Group VI metal carbonyl complexes containing a metal—metal triple bond [1, 2]. For example, phosphites, phosphines, and carbon monoxide add, one to each metal atom of I, to give the metal—metal single bonded complexes II (L = $P(OR)_3$, PR_3, CO),



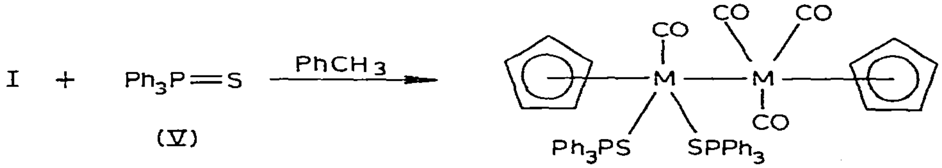
---

*E.W.R. Steacie Fellow.

while metallotetrahedrane complexes (3) are formed on addition of alkynes. Recently, we found that thioketones react in a facile manner with 1 to give 4, which contains a metallothiocyclopropane unit and a semi-bridging carbonyl group.

There has been considerable interest in the reactions of phosphine sulfides with organometallic compounds [3—7]. We believed that the reaction of an organic substrate containing a P=S unit with I, M = Mo, W merited examination since one could conceive of the production of II, L = $R_3P=S$, or the phosphine sulfide analog of IV. This communication describes the unexpected results of this study.

Treatment of I, M = Mo, with triphenylphosphine sulfide (V, 1.15/1.0 mol ratio of V/I) in refluxing toluene for 2.5 h results in the formation of the purple, air-sensitive complex VI, M = Mo, m.p. 118—120°C in which both added phosphine sulfide ligands are attached to the same molybdenum atom. Structure VI, M = Mo, was elucidated on the basis of analytical, molecular weight (osmometry), and spectral data. The proton magnetic resonance spectrum was definitive giving, in addition to the absorptions for the aromatic protons, two signals for the cyclopentadienyl groups, one appearing as a singlet at δ 5.12 ppm, while the other occurred as a triplet (coupling with two phosphorus atoms) at δ 4.78 ppm (J(P—H) 0.8 Hz) [8]. Metal carbonyl stretching bands appeared in the infrared ($CHCl_3$) at 1972, 1894, and 1819 cm^{-1}.



(V)

(VI)

The tungsten complex, I M = W, reacted with triphenylphosphine sulfide (V) in a similar manner to I, M = Mo, affording the pink-red complex VI, M = W, m.p. 133—134°C (IR(CH_2Cl_2) ν(CO) 1970, 1882, 1814 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.87 (t, C_5H_5, J(P—H) 0.7 Hz), 5.16 (s, 5H, C_5H_5), 7.3—7 ppm (m, 30H, aromatic protons).

The fully methylated complex $[(CH_3)_5C_5Mo(CO)_2]_2$ [9], failed to react with triphenylphosphine sulfide, even on refluxing in toluene or 1/1 toluene/xylene for 64 h.

The formation of complex VI represents a net 1,1-addition of triphenylphosphine sulfide to I. Whether this, to our knowledge, unprecedented process occurs via: (i) the phosphine sulfide analog of IV; (ii) generation of II, L = Ph_3PS and subsequent rearrangement; (iii) or an alternate route, remains to be determined.

Acknowledgement

We are grateful to the Natural Sciences and Engineering Research Council for support of this work.

References

1 M.D. Curtis and R.J. Klingler, J. Organometal. Chem., 161 (1978) 23, and references cited therein.
2 H. Alper, N.D. Silavwe, G.I. Birnbaum, and F.R. Ahmed, J. Amer. Chem. Soc., 101 (1979) 6582, and references cited therein.
3 S.O. Grim and J.D. Mitchell, Inorg. Chem., 16 (1977) 1762.
4 F. Mathey and F. Mercier, J. Organometal. Chem., 177 (1979) 255.
5 F. Mathey and C. Santini, Can. J. Chem., 57 (1979) 723.
6 F. Mathey and G. Sennyey, J. Organometal. Chem., 105 (1976) 73.
7 E.W. Ainscough, A.M. Brodie, and A.R. Furness, J. Chem. Soc., Dalton, (1973) 2360.
8 R.J. Haines and C.R. Nolte, J. Organometal. Chem., 24 (1970) 725.
9 R.B. King, M.Z. Iqbal and A.D. King, Jr., J. Organometal. Chem., 171 (1979) 53.