Reactivity of Co-ordinated S_2CPR_3 Ligands. Crystal and Molecular Structure of $[Mo\{\eta^3\text{-}SC(SMe)PMe_3\}(CO)_2(PMe_3)_2]I$

Agustín Galindo,[a] Enrique Gutiérrez-Puebla,*,[b] Angeles Monge,[b] Miguel Angel Muñoz,[a] Antonio Pastor,[a] Caridad Ruiz[b] and Ernesto Carmona*,[a]

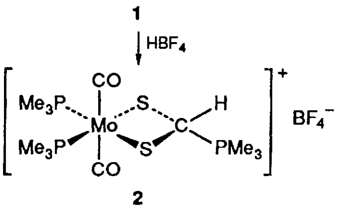
[a] *Departamento de Química Inorgánica-Instituto de Ciencias de Materiales, Universidad de Sevilla-C.S.I.C., Aptdo. 553, 41071 Sevilla, Spain*

[b] *Facultad de Ciencias Químicas-Instituto de Ciencias de Materiales, Universidad Complutense de Madrid-C.S.I.C., 28040 Madrid, Spain*

Treatment of $[Mo(S_2CPMe_3)(CO)_2(PMe_3)_2]$ **1** with HBF_4 or RI affords respectively $[Mo\{S_2C(H)PMe_3\}(CO)_2(PMe_3)_2]BF_4$ **2** and $[Mo\{\eta^3\text{-}SC(SR)PMe_3\}(CO)_2(PMe_3)_2]I$ (R = Me **3a** or Et **3b**); an X-ray study of **3a** shows that alkylation takes place at sulfur and that the resulting phosphoniodithioester ligand is trihapto (*S,S′,C*) bonded to molybdenum.

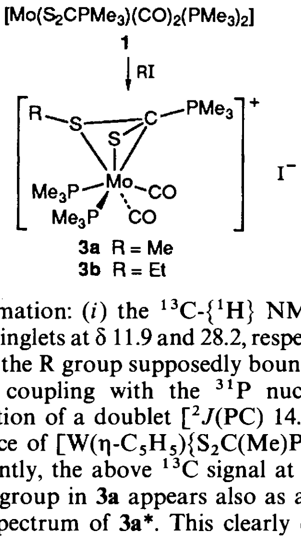
Complexes containing zwitterionic, trialkylphosphonium dithiocarboxylate ligands, S_2CPR_3, have attracted considerable attention in recent years and a variety of co-ordination modes for these ligands has been demonstrated by X-ray crystallography in both mono- and bi-nuclear complexes.[1] The chemistry of these compounds, in particular the reactivity of the co-ordinated S_2CPR_3 group, remains less understood, although there is ample evidence indicating electrophilic character of the central carbon atom.[2] In this contribution we report on the behaviour of the recently prepared[3] $[Mo(S_2CPMe_3)(CO)_2(PMe_3)_2]$ **1** towards electrophiles X^+ (X = H, Me or Et). This has allowed the isolation of two types of products, a complex of composition $[Mo\{S_2C(H)PMe_3\}(CO)_2(PMe_3)_2]BF_4$ **2** and two closely related derivatives $[Mo\{\eta^3\text{-}S,C,S'\text{-}SC(SR)PMe_3\}(CO)_2(PMe_3)_2]I$ (R = Me **3a** or Et **3b**). Compounds **3** constitute a rare example[4] of complexes of *S*-alkyl phosphoniodithioester ligands, $S{=}C(SR)PMe_3$.

Treatment of **1** with HBF_4 affords red crystals[†] of the cationic complex **2** [equation (1)]. Characterization of the $Me_3PC(H)S_2^-$ ligand is straightforward on the basis of the available spectroscopic data. In particular, the C-bound hydrogen atom gives a ^1H NMR doublet at δ 6.34 [^2J(HP) 4.5 Hz], while the central carbon provides a ^{13}C resonance centred at δ 64.9 [^1J(CH) 156, ^1J(CP) 46, ^3J(CP) 4 Hz].



2 (1)

The reaction of **1** with RI (R = Me or Et) yields orange or red crystals[‡] of the corresponding derivatives **3a** (R = Me) or **3b** (R = Et). Similarly to **2**, compounds **3** behave as 1:1 electrolytes. Their $^{31}P\text{-}\{^1H\}$ NMR spectra display typical AMX spin systems in accord with the presence of two non-equivalent co-ordinated PMe_3 ligands and a quaternary phosphorus atom (data for **3a**: δ_A 44.1, δ_M 3.3, δ_X −10.1 [$^3J_{AM}$ 6, $^3J_{AX}$ 2, $^2J_{MX}$ 50 Hz]). NMR data seem to be in accord with a formulation for **3** similar to that proposed for **2**, *i.e.* as derivatives of a trimethylphosphonium dithiocarboxylate ligand, $Me_3PC(R)S_2$. Although compounds of this type are already known,[2a,5] a closer examination of the ^{13}C NMR spectra of **3** and **3a*** (*ca.* 33% enriched[‡] in $^{13}CS_2$) reveals some discrepancies with a structure of this type, and further suggests that alkylation takes place at one of the sulfurs rather than at the carbon atom [equation (2)]. Such a proposal is based on the following pieces of information: (*i*) the $^{13}C\text{-}\{^1H\}$ NMR spectra of **3a** and **3b** exhibit singlets at δ 11.9 and 28.2, respectively, due to the carbon atom of the R group supposedly bound to the CS_2 carbon. The lack of coupling with the ^{31}P nucleus contrasts with the observation of a doublet [^2J(PC) 14.7 Hz] for the analogous resonance of $[W(\eta\text{-}C_5H_5)\{S_2C(Me)PMe_3\}(CO)_2]$;[5] (*ii*) more importantly, the above ^{13}C signal at δ 11.9, corresponding to the Me group in **3a** appears also as a singlet in the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **3a***. This clearly demonstrates that the R group is not bonded to the CS_2 carbon.



(2)

3a R = Me
3b R = Et

[†] An excess of HBF_4 (0.9 mmol) was added to a stirred solution of **1** (0.29 g, *ca.* 0.65 mmol) in Et_2O (100 cm^3) to produce a red solid. After stirring for 30 min at room temperature the solid was filtered off, washed with Et_2O (2 × 20 cm^3) and recrystallized from acetone. Red crystals of **2** (0.17 g) were collected in 48% yield (Found: C, 26.7; H, 5.0. $C_{12}H_{28}BF_4MoO_2P_3S_2$ requires C, 26.5; H, 5.15%). Selected spectroscopic data for **2**: ν_{max}/cm^{-1} (CO) 1950 and 1840 (Nujol); $\delta_H(CD_2Cl_2)$ 6.34 [d, J(HP) 4.5 Hz, $S_2CH(PMe_3)$]; $^{13}C\text{-}\{^1H\}$ NMR (CD_2Cl_2), δ 64.9 [dt, ^1J(CP) 46, ^3J(CP) 4 Hz, $S_2CH(PMe_3)$].

[‡] A solution of **1** (0.4 g, 0.9 mmol) in Et_2O (30 cm^3) was treated with MeI (1.8 cm^3 of a *ca.* 1 mol dm^{-3} solution in toluene). A yellow-orange solid slowly precipitated and was collected after 4 h of stirring, washed with Et_2O and recrystallized from acetone–Et_2O. Yield of **3a**: 0.24 g, 45% (Found: C, 26.4; H, 4.9. $C_{13}H_{30}IMoO_2P_3S_2$ requires C, 26.1; H, 5.0%). Selected spectroscopic data for **3a**: ν_{max}/cm^{-1} (CO) 1925 and 1850 (Nujol); $\delta_H(CD_2Cl_2)$ 2.06 [br d, J(HP) 1.3 Hz, SCH_3]; $\delta_P(CD_2Cl_2)$ −10.1 [dd, ^2J(PP) 50, ^3J(PP) 2, PMe_3], 3.3 [dd, ^2J(PP) 50, ^3J(PP) 6, PMe_3] and 44.1 [dd, ^3J(PP) 6, ^3J(PP) 2 Hz, $SC(SMe)PMe_3$]; $^{13}C\text{-}\{^1H\}$ NMR (CD_2Cl_2), δ 11.9 (s, SCH_3). A sample of **3a**, *ca.* 33% enriched in $^{13}CS_2$ (**3a***) was prepared similarly starting from **1*** (see ref. 3). $^{13}C\text{-}\{^1H\}$ NMR (CD_2Cl_2): δ 11.9 (s, SCH_3) and 66.6 [d, ^1J(CP) 87 Hz, $SC(SMe)PMe_3$].

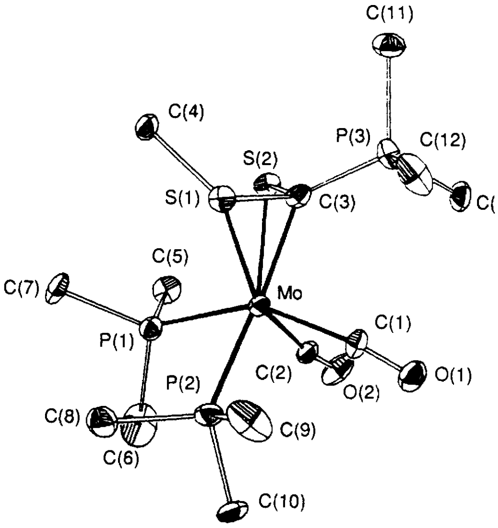


Fig. 1 Molecular structure of the cation $[Mo\{\eta^3\text{-}SC(SMe)PMe_3\}(CO)_2(PMe_3)_2]^+$ of complex **3a** showing the atom numbering scheme. Selected bond distances (Å) and angles (°): Mo–S(1) 2.567(8), Mo–S(2) 2.506(2), Mo–C(3) 2.125(6), S(1)–C(3) 1.793(6), S(2)–C(3) 1.727(7), S(1)–C(4) 1.791(5), S(1)–C(3)–S(2) 117.3(3), S(2)–C(3)–P(3) 119.3(4), S(1)–C(3)–P(3) 117.5(5), C(3)–S(1)–C(4) 106.1(3)

In order to confirm the site of attack of the alkyl group and to ascertain the co-ordination mode of the methylated ligand an X-ray study of **3a** has been undertaken. An ORTEP[6] perspective view of the molecules of **3a** is shown in Fig. 1, which includes also some relevant bond distances and angles.† As can be seen, alkylation of the Me_3PCS_2 group takes place at one of the sulfur atoms to yield a trimethylphosphonium dithioester ligand, trihapto bonded to molybdenum through the carbon and the two sulfur atoms of the CS_2 group. This is an unprecedented co-ordination mode for this type of ligand, of which only two related examples are, to our knowledge, known: the nickel complex $[Ni\{SC(SMe)PPh_2CH_2CH_2N(CH_2CH_2PPh_2)_2\}]$, having an (*S,C*)-$R_3PC(SMe)S$ group[4a] and the recently reported binuclear species $[Mn_2(CO)_6(\mu\text{-}H)\{\mu\text{-}SC(SR')PR_3\}]$ which contains a bridging (*S,S'*),(*S',C*)-dithioester ligand.[4b] *S,S',C* Co-ordination of the CS_2 group of other related ligands is known.[1,10–13]

A possible, and otherwise useful, representation of the molecules of **3a** is as a severely distorted square pyramid, with the sulfur-containing ligand in the apical position [the dihedral angle between the S,S′,C plane and the best mean-square plane containing atoms P(1), P(2), C(1) and C(2) is 165°]. The Mo–C(3) distance of 2.125(6) Å compares well with that found in complexes of η^3-dithioester ligands {*e.g.* 2.154(8) Å in $[W\{\eta^3\text{-}SC(Me)(SMe)\}(CO)_3(PPr^i{}_3)]$}.[12d] Other structural parameters are also normal and require no additional comments at this preliminary stage.

In view of literature precedents it seems likely that complex **2** forms by protonation at the electron-rich molybdenum centre of **1** followed by hydride transfer to the CS_2 carbon.[2] As for **3**, alkylation may occur directly at sulfur and in fact unstable $[SC(SR')PR_3]^+X^-$ species can be obtained by alkylation of the corresponding S_2CPR_3 adducts.[14] The extension of these results to other related systems is now in progress.

Acknowledgements

We thank the Spanish Ministry of Education (A. P.) for a research studentship and gratefully acknowledge financial support from Dirección General de Investigación Cientifica y Tecnica (Proyecto PB-87201) and Junta de Andalucía. Thanks are also due to the University of Sevilla for use of analytical and NMR facilities, and to one of the referees for correcting the choice of space group.

References

1 See, for example, D. Miguel, V. Riera, J. A. Miguel, M. Gómez and X. Solans, *Organometallics*, 1991, **10**, 1683 and refs. therein.

2 (*a*) C. Bianchini, A. Meli, P. Dapporto, A. Tofanari and P. Zanello, *Inorg. Chem.*, 1987, **26**, 3677; (*b*) C. Bianchini, C. Mealli, A. Meli and G. Scapacci, *Organometallics*, 1983, **2**, 141; (*c*) C. Bianchini, A. Meli and A. Orlandini, *Inorg. Chem.*, 1982, **21**, 4161.

3 E. Carmona, A. Galindo, A. Monge, M. A. Muñoz, M. L. Poveda and C. Ruiz, *Inorg. Chem.*, 1990, **29**, 5074.

4 (*a*) C. Bianchini, C. A. Ghilardi, A. Meli and A. Orlandini, *J. Organomet. Chem.*, 1984, **270**, 251; (*b*) B. Alvarez, S. García-Granda, Y. Jeannin, D. Miguel, J. A. Miguel and V. Riera, *Organometallics*, 1991, **10**, 3005.

5 F. R. Kreissl, N. Ullrich, A. Wirsing and U. Thewalt, *Organometallics*, 1991, **10**, 3275.

6 C. K. Johnson, ORTEP II, Oak Ridge National Laboratory, TN, 1971.

7 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 72–98.

8 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

9 J. M. Stewart, XRAY 80 System, Computer Science Center, University of Maryland, College Park, MD, 1985.

10 C. Bianchini, C. A. Ghilardi, A. Meli, S. Midolini and A. Orlandini, *Organometallics*, 1982, **1**, 778.

11 E. Carmona, A. Galindo, E. Gutiérrez-Puebla, A. Monge and C. Puerta, *Inorg. Chem.*, 1986, **25**, 3804; E. Carmona, A. Galindo, C. Guille-Photin, R. Laï, A. Monge, C. Ruiz and L. Sánchez, *Inorg. Chem.*, 1988, **27**, 488; E. Carmona, E. Gutiérrez-Puebla, A. Monge, P. J. Pérez and L. Sánchez, *Inorg. Chem.*, 1989, **28**, 2120.

12 (*a*) J. Hyde, K. Venkatasubramanian and J. Zubieta, *Inorg. Chem.*, 1978, **17**, 414; (*b*) M. Tatsumisago, G. Matsubayashi, T. Tanaka, S. Nishigaki and K. Nakatsu, *J. Chem. Soc., Dalton Trans.*, 1982, 121; (*c*) M. I. Bruce, T. W. Hambley, M. R. Snow and G. A. Swincer, *J. Organomet. Chem.*, 1984, **273**, 361; (*d*) W. A. Schenk, D. Rüb and C. Burschka, *J. Organomet. Chem.*, 1987, **328**, 287, 305; (*e*) F. Scott, G. J. Krugger, S. Cronje, A. Lombard, H. G. Raubenheimer, R. Benn and A. Rufinska, *Organometallics*, 1990, **9**, 1071.

13 L. L. Wright, R. C. Haltiwanger, J. Noordik and M. DuBois Rakowski, *J. Am. Chem. Soc.*, 1987, **109**, 282, 283; B. Alvarez, D. Miguel, V. Riera, J. A. Miguel and S. García-Granda, *Organometallics*, 1991, **10**, 384; D. Miguel, J. A. Pérez-Martínez, V. Riera and S. García-Granda, *J. Organomet. Chem.*, 1991, **420**, C12.

14 K. A. Jensen and P. H. Nielsen, *Acta. Chem. Scand.*, 1963, **17**, 547.

Received 12*th May* 1992; *Communication* 2/02463B

---

† *Crystal data.* $C_{13}H_{30}IMoO_2P_3S_2$, M = 598.3, triclinic, space group $P\bar{1}$, a = 11.193(2), b = 12.988(7), c = 8.791(4) Å, α = 99.81(4), β = 94.54(5), γ = 78.11(4)°, U = 1231.0(9) Å^3, Z = 2, D_c = 1.61 g cm^{-3}, F(000) = 592, μ(Mo-Kα) = 21.2 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å, 295 K, Enraf-Nonius CAD4 diffractometer, ω–2θ scan technique. The cell dimensions were refined by least-squares fitting of the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects, 4780 reflections measured, 3909 [$I \geqslant 2\sigma(I)$] used in the refinement. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo, S, P and I were taken from ref. 7. The structure was solved by Patterson and Fourier methods. Empirical absorption corrections[8] were applied at the end of the isotropic refinement. Final refinements were fixed isotropic factors and coordinates for H atoms. Most of the calculations were carried out with the XRAY 80 system.[9] Final R 0.034 and R' 0.038 (unit weights). Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.