A New Synthesis of Phosphine-substituted *cis*-1,2-Disubstituted-ethylene-1,2-dithiolate Complexes and some Related Reactions

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THE recent interest in *cis*-1,2-disubstituted-ethylene-1,2-dithiolate complexes has centred on their magnetic properties,[1] redox behaviour,[2] spectra, structures,[3] and attempts to elucidate their detailed electronic configurations.[4] The previous syntheses, in both the bis- and tris-series, utilised transition-metal carbonyls as precursors for the perfluoromethyl derivatives. We now report a more convenient procedure which is especially useful for those metals whose carbonyls are unknown or difficult to prepare. A halogeno-triphenylphosphine complex (1 mol.) is refluxed in benzene with bisperfluoromethyl-1,2-dithieten (3·5 mol.); the latter reagent is, in part, desulphurised and removes the co-ordinated phosphine as triphenylphosphine sulphide. The complexes are isolated as previously described.[2] Typical reactions are: $[(C_6H_5)_4As]_2\,[NiS_4C_4(CF_3)_4]$ (50% from $[(C_6H_5)_3P]_2NiBr_2$), $[(C_6H_5)_4As]_2[PdS_4C_4(CF_3)_4]$ (60% from $[(C_6H_5)_3P]_2PdCl_2$). The copper and gold complexes have been prepared for the first time, $[(C_6H_5)_4As][AuS_4C_4(CF_3)_4]$ pale green, m.p. 179·5—

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† Satisfactory elemental analyses were obtained for all new compounds reported.

[1] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Amer. Chem. Soc.*, 1963, **85**, 2029.

[2] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 1963, **2**, 1227; 1964, **3**, 814.

[3] J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 1964, **3**, 1500, 1507. R. Eisenberg and J. A. Ibers, *Inorg. Chem.* 1965, **4**, 605.

[4] A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, 1964, **86**, 4580. A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, 1964, **86**, 2799. S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *ibid.*, 1964, **86**, 4594.

181° (70% from $(C_6H_5)_3PAuCl$),† $[(C_6H_5)_4As]_2[CuS_4C_4(CF_3)_4]$red–brown, m.p. 198—200° (from $[(C_6H_5)_3PCuI]_4$).

The isolation of the copper complex enables a limited comparison to be made between the ease of oxidation of the copper complexes and those of nickel as a function of the ligand substituent R. An examination of the half-wave potentials[2,5] for the couple

$$(MS_4C_4R_4)^{2-} \rightleftharpoons (MS_4C_4R_4)^- + e$$

shows that for M=Ni the ease of oxidation is $R = H \sim alkyl > C_6H_5 \gg CF_3 > CN$. Paramagnetic resonance studies[4] show that the electronic configuration of the mono-anion in this case is consistent with the removal of an electron from the $\pi^*(b_{3g})$ molecular orbital (mainly d_{yz}), but for M=Cu the electron is removed from the $\sigma^*(b_{1g})$ orbital (mainly d_{xy}) and might reasonably have been expected to be much less dependent upon R. The relevant half-wave potentials[6] show that this is not the case: M=Ni, R=CN, 0·226; $R=CF_3$, −0·121; R=H, −0·915. M=Cu, R=CN, 0·330; $R=CF_3$, 0·010.

Under aprotic conditions $(C_6H_5)_3PAuCl$ and bis-perfluoromethyl-1,2-dithieten give the novel gold complex $(C_6H_5)_3PAu(Cl)(S_4C_4(CF_3)_4)$, olive green, m.p. 145·5—147°. It is reduced rapidly, by solvents containing oxygen or nitrogen functions, to $[AuS_4C_4(CF_3)_4]^-$ with loss of triphenylphosphine and chloride ion. It can be formulated as either a six- or a five-co-ordinate complex. The latter formulation prompted us to attempt the synthesis of the isoelectronic platinum species. Triphenylphosphine with $[PtS_4C_4(CF_3)_4]$ gave, instead of the expected adduct, the known[2] $[(C_6H_5)_3P]_2PtS_2C_2(CF_3)_2$ and triphenylphosphine sulphide, the analogous nickel species reacted similarly. This behaviour is in direct contrast to that found for weak organic oxygen- or nitrogen-functional bases, *viz.* reduction to the $[MS_4C_4(CF_3)_4]^-$ anions.[2] Finally these reactions are in direct contrast to those reported by Schrauzer[7] for $[MS_4C_4R_4]$ (M=Pd,Pt, $R=CH_3,C_6H_5$) with triphenylphosphine to give six-co-ordinate complexes $[(C_6H_5)_3P]_2MS_4C_4R_4$. We have re-investigated these adducts and find them to be the expected four-co-ordinate complexes, *e.g.* $[(C_6H_5)_3P]_2PtS_2C_2(C_6H_5)_2$.

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[5] E. Hoyer and W. Schroth, *Chem. and Ind.* 1965, 652.

[6] Polarographic half-wave potentials, in volts, s.c.e. reference, acetonitrile solution, 10^{-3}M complex, 0·05M in supporting electrolyte.

[7] G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, 1965, **87**, 1483.