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Reaction of Some Bidentate Phosphorus and Arsenic Donor Ligands with Tris(dimethylphosphorodithioato)$\mathrm{Co^{III}}$ and $\mathrm{Rh^{III}}$

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Monodentate tertiary phosphines react with Ni(S$_2$P(OR)$_2$)$_2$ complexes to give five-coordinate adducts [1], whereas the $\mathrm{Pd^{II}}$ and $\mathrm{Pt^{II}}$ analogues form square planar complexes in which one of the $^{-}$S$_2$P(OR)$_2$ ligands is monodentate [2] or substituted by two phosphine ligands [3]. Only with bidentate N-ligands, such as 2,9-dimethylphenanthroline, do Ni(S$_2$P(OR)$_2$)$_2$ complexes appear to give adducts containing monodentate $^{-}$S$_2$P(OR)$_2$ [4]. Attempts to obtain the latter, using bidentate phosphine- and arsine- containing ligands (dppe and dpae*), instead lead to [Ni(S$_2$P(O)OMe)(dppe)] and [Ni(S$_2$P(O)OMe)(dpae)] [5].

We now report that Co(mpt)$_3$ and Rh(mpt)$_3$ also react with dppe and dpae to form complexes with the unusual ligand $^{2-}$S$_2$P(O)OMe.

The phosphines and arsines were Strem products and were used as received. Co(mpt)$_3$ and Rh(mpt)$_3$ were prepared by standard methods and characterised by elemental analysis (C, H, P, and S by G. Berhardt, and Co by EDTA titration after destruction of organic matter) and electronic spectra [6].

M(S$_2$P(O)OMe)(mpt)(dppe) (M = Co, Rh)

Co(mpt)$_3$ (1 mmol) and dppe (1 mmol) were refluxed in 50 ml of acetone for 1 h and the mixture filtered hot. Cooling gave the complex as green microcrystals which were recrystallised from acetone. The $\mathrm{Rh^{III}}$ analogue required longer reflux times (Co 4h, Rh 3 days). Reaction with ligands in excess gave the same products.

Although reflux of dae and Co(mpt)$_3$ or Rh(mpt)$_3$ leads to colour changes in the mixture, only starting products could be isolated. Analyses and some spectra are given in the Table.

Apart from the elemental analyses, evidence that demethylation of one of the mpt ligands has, indeed, occurred comes from IR and ESCA spectra. The O(1s) region in the ESCA spectra of the cobalt complexes showed a reproducible shoulder to higher kinetic energy, as compared to a single peak in Co(mpt)$_3$ itself, characteristic of a more negative oxygen atom [7]. The IR spectra of the complexes show a peak at 1190 cm^{-1} characteristic of ν(P=O) [8].

The complexes are soluble in CHCl$_3$, MeOH, and CH$_2$Cl$_2$ and insoluble in benzene and dioxan. Attempts to isolate possible charged intermediates as was done for a similar product, [Pt(S$_2$P(OEt)$_2$)(PPh$_3$)$_2$]$^+$ [2], by reaction with NaBPh$_4$ and cooling, were unsuccessful.

There is evidence for the presence of such an intermediate from measurements of conductance *vs.* time (see Figure). In acetone, there is a steep rise in conductance during reaction between Co(mpt)$_3$ and dpae to a peak with conductance *ca.* 30% that for a uni–univalent salt (Ph$_4$AsCl) under the same condi-

TABLE. Analytical and Spectral Data.

Compound	Colour	C	H	P	S	M	Electronic spectra (kK)^a
Co(mpt)(dppe)- (S$_2$P(O)OMe)	dark green	38.6 (44.2)	4.2 (4.1)	–	–	7.6 (7.8)	16.4 (840); 23.3 (1700)
Co(mpt)(dpae)- (S$_2$P(O)OMe)	dark green	43.7 (43.8)	4.2 (4.2)	11.4 (11.6)	16.2 (16.2)	7.6 (7.4)	15.7 (960); 24.4 (3500)
Rh(mpt)(dppe) (S$_2$P(O)OMe)	yellow orange	43.3 (43.5)	4.2 (4.1)	15.6 (15.5)	16.1 (16.0)	–	25.3 (1300); 27.4 (1600)
Rh(mpt)(dpae) (S$_2$P(O)OMe)	yellow orange	37.4 (41.3)	3.9 (3.9)	11.7 (11.0)	16.3 (16.2)	–	24.5 (1600); 27.0 (1700)

^{a} ϵ (M^{-1} cm^{-1}) in parentheses.

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*Abbreviations: mpt$^-$ = $^{-}$S$_2$P(OMe)$_2$; dppe = Ph$_2$PC$_2$H$_4$PPh$_2$; dpae = Ph$_2$PC$_2$H$_4$AsPh$_2$; dae = Ph$_2$AsC$_2$H$_4$AsPh$_2$.

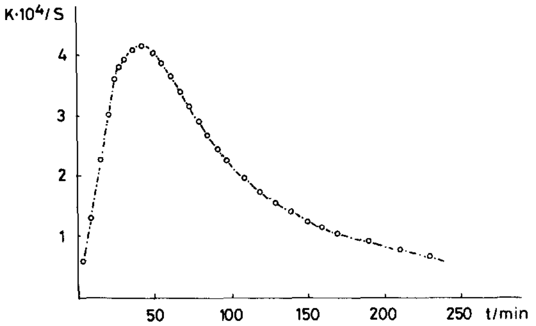
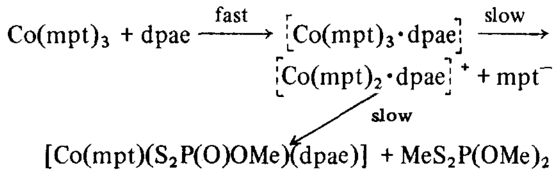


Figure. Conductance *vs.* time plot for $\mathrm{Compt_3}$ + dpae (mol ratio 1:10; $[\mathrm{Compt_3}] = 1 \times 10^{-3}$ mol dm^{-3}) in acetone.

tions, after 50 min. The decrease in conductance is much slower, going to *ca.* 0 only after 10 h. Solvents of dielectric constant lower than that of acetone drastically lower the conductance, which is also relatively insensitive to $\mathrm{Co(mpt)_3}$: dpae ratio in the ascending part of the curve, but changes sensibly after the peak.

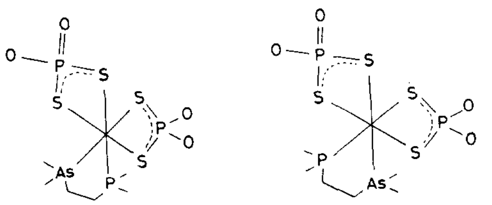
Preliminary kinetic measurements, performed following the disappearance of the 770 nm band in $\mathrm{Co(mpt)_3}$ and the appearance of that at 640 nm (under pseudo-first-order conditions) in acetone provide little clear evidence of any other intermediates which might be involved. However, the only small shift in the band (from 610 to 640 nm) suggests the intermediate has a chromophore similar to that of the final product. A reasonable mechanism from the data obtained to date is:



$$\mathrm{Co(mpt)_3 + dpae} \xrightarrow{\text{fast}} [\mathrm{Co(mpt)_3 \cdot dpae}] \xrightarrow{\text{slow}} [\mathrm{Co(mpt)_2 \cdot dpae}]^+ + \mathrm{mpt}^-$$

$$\xrightarrow{\text{slow}} [\mathrm{Co(mpt)(S_2P(O)OMe)(dpae)}] + \mathrm{MeS_2P(OMe)_2}$$

Two isomers are possible:



But other confomers are also possible because of the generation of the asymmetric centre on demethylation. A crystal structure and kinetic analysis is under way.

Acknowledgment

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