

Preliminary communication

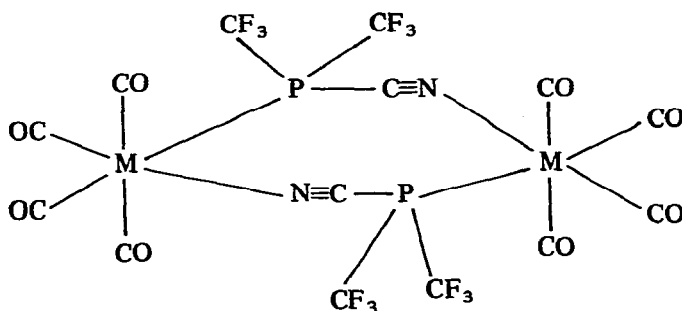
Metal carbonyl complexes containing a bridging cyanophosphine ligand

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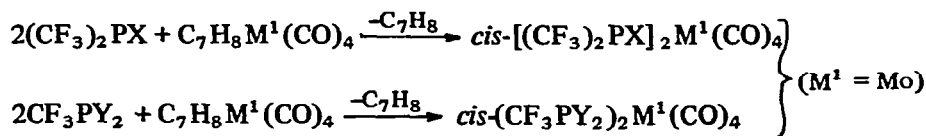
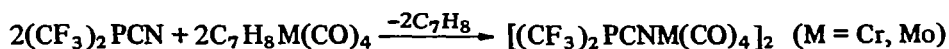
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It is well known that thiocyanate ion can act as a bridging group between two metal atoms¹. We have now synthesised the first examples of dimeric complexes (I) involving a bridging cyanophosphine ligand which contains a new eight-membered ring system.



(I, M = Cr, Mo)

The yellow solid compounds which are readily obtained by displacement of norbornadiene from $C_7H_8M(CO)_4$ ($M = Cr, Mo$) by treatment with bis(trifluoromethyl)cyanophosphine (room temperature, $M = Mo$; 60° , $M = Cr$), can be sublimed with difficulty and decompose in solution. Similar reactions with other trifluoromethyl phosphines $(CF_3)_2PX$ and CF_3PY_2 ($X = H, F, Cl, Br, I, NMe_2$; $Y = H, F, Cl, Br$) afford monomeric *cis*- $[(CF_3)_2PX]_2M^1(CO)_4$ and *cis*- $(CF_3PY_2)_2M^1(CO)_4$ respectively^{2,3}.



The identity of (I) was established by elemental analyses, (M = Cr: Found: C, 23.3; H, 0.2; N, 3.9; P, 8.8; F, 31.8, Cr, 14.7. $(\text{CrC}_7\text{F}_6\text{PNO})_n$ calcd.: C, 23.4; H, 0.0; N, 3.9; P, 8.4; F, 31.8; Cr, 14.5%. M = Mo: Found: C, 20.8; H, 0.0; N, 3.7; P, 7.8; F, 27.8; Mo, 24.7. $(\text{MoC}_7\text{F}_6\text{PNO}_4)_n$ calcd.: C, 20.9; H, 0.0; N, 3.5; P, 7.7; F, 28.3; Mo, 23.8%), and the dimeric structure is suggested by the observation of the parent ions in the mass spectra. The C-N stretching frequency in the complexes is about 40 cm^{-1} lower than the free ligand value.

The stability of the eight-membered ring system is indicated by the fragmentation pattern in the mass spectrum which shows a stepwise loss of all eight carbonyl groups while the $(\text{MPCN})_2$ ring system remains intact. All the atoms of the eight-membered ring in $\text{Pt}_2(\text{PPr}_3)_2\text{Cl}_2(\text{SCN})_2$ (II) are known to be coplanar⁴ and it has been suggested that there may be interaction between metal *d*-electrons and π -orbitals of the ring system. By analogy with (II) we have written the most symmetrical structure for (I) but at present we cannot rule out the alternative structure in which both phosphorus atoms are bonded to the same metal and further studies are in progress.

ACKNOWLEDGEMENT

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