Crystal Structure of a Tri-tertiary Phosphine Complex of Manganese(I) and Chromium(0)

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Summary The preparation of two isomers (A and B) of the novel hetero-bimetallic species, $Br(CO)_3Mn(triphos)Cr(CO)_5$, is described; the crystal structure of A has been determined by three-dimensional X-ray diffraction.

VARIOUS metal complexes containing poly-tertiary phosphines such as $PPh(CH_2CH_2PPh_2)_2$,(triphos), have been synthesized.[1-4] We report the preparation and crystal structure of the first example of a new class of these complexes.

Treatment of $Mn(CO)_5Br$ with (triphos) (1 : 1 mol ratio) in refluxing chloroform for 1½ h gives the yellow neutral tricarbonyl species, $Mn(CO)_3(triphos)Br$, in high yield. The (triphos) ligand in this complex is believed to be coordinated to the manganese atom through only two of its three phosphorus atoms. Moreover, the presence of three strong C–O stretching absorptions in its i.r. spectrum (Table) suggests a mutually *cis* stereochemistry for the three CO groups. T.l.c. of this *cis*-$Mn(CO)_3(triphos)Br$ product shows it to be a mixture of *two* complexes which cannot be separated on a preparative scale. However, reaction of the mixture with $Cr(CO)_5THF$ in tetrahydrofuran (THF) for 12 h affords two orange products (A and B) which are readily separable by preparative t.l.c. using benzene as eluent—(A) having the larger R_f value in this solvent. Elemental analyses for *both* (A) and (B) are in excellent agreement with the hetero-bimetallic formulation, $Br(CO)_3Mn(triphos)Cr(CO)_5$. The decomposition points of the two complexes are very similar: (A), 96—100; (B), *ca.* 85°. Moreover, their i.r. spectra in the C-O stretching region are virtually identical (Table) and are essentially superpositions of the spectra of *cis*-$Mn(CO)_3$(triphos)Br and $Cr(CO)_5THF$.

Complex (A) crystallizes from CH_2Cl_2–n-hexane mixtures as orange needles in the space group *Pbcn* with cell parameters: $a = 21{\cdot}260(6)$, $b = 14{\cdot}451(3)$, $c = 28{\cdot}338(9)$ Å; $V = 8{,}710$ Å^3; $Z = 8$; $D_c = 1{\cdot}44$ g cm^{-3} [$D_{obs} = 1{\cdot}44$ g cm^{-3} (in ZnI_2)]. *X*-Ray data were collected on a Picker FACS-I diffractometer (graphite monochromated Cu-K_α radiation; $\lambda = 1{\cdot}5418$ Å). Of the 3,789 symmetry independent reflections which were collected, 1,324 were considered observed ($I > 2\sigma$). The data were corrected for decomposition because the crystal decomposed gradually upon *X*-ray irradiation. No absorption corrections ($\mu = 73{\cdot}0$) were made. Block diagonal least-squares refinement of the observed data, using anisotropic corrections for the non-carbon and non-oxygen atoms, led to a conventional *R* factor of 0·099. The molecular structure of (A) is shown in the Figure.

TABLE. *I.r. spectra in the C–O stretching region of the new (triphos) complexes (in* CH_2Cl_2 *solution)*

Complex	ν_{CO} (cm^{-1})				
cis-$Mn(CO)_3$ (triphos)Br[a]	2021s	1954s	1911s		
A	2063w	2022s	1981s	1940vs	
B	2064w	2024s	1982s	1935vs	1914sh

[a] Mixture of two isomers (see text).

The *X*-ray data confirm the proposed stoichieometric formula of (A). The two approximately octahedral metal carbonyl moieties are linked together through the phosphorus atom, P(3), which is presumably the unco-ordinated phosphorus atom in the original *cis*-$Mn(CO)_3$(triphos)Br species. The only other known example of this type of hetero-bimetallic complex is the cobalt-iron complex $(NO)(CO)_2Co(Ph_2PCH_2CH_2PPh_2)Fe(CO)(NO)_2$.[5]

The three CO groups in the $Br(CO)_3Mn$(triphos) moiety are mutually *cis* to each other, as would be expected if the original $Mn(CO)_3$(triphos)Br species has the same stereochemistry, as was suggested earlier. The phenyl group Ph(3), on phosphorus atom, P(2), is *trans* to Br with respect to the Mn–P(1)–P(2)–C(3)–C(1) plane. This is a particularly interesting feature of the structure because it is felt that the stereochemistry of this phenyl group provides the key to the formation of (A) and (B). Owing to its greater basicity and presumably lower steric hindrance, P(2) is expected to be the first of the three phosphorus atoms in (triphos) to co-ordinate to the manganese atom during the formation of *cis*-$Mn(CO)_3$(triphos)Br from $Mn(CO)_5Br$.[2] However, P(2) can approach the manganese atom with its phenyl ring *cis* or *trans* to Br. No matter which one of the two remaining phosphorus atoms co-ordinates next, there are two possible isomers of *cis*-$Mn(CO)_3$(triphos)Br. On reaction with $Cr(CO)_5THF$, these isomers then give rise to isomers (A) and (B) of $Br(CO)_3Mn(triphos)Cr(CO)_5$. A somewhat related type of isomerism has been described recently for platinum and palladium complexes of Me(Ph)-$AsCH_2CH_2As$(Ph)Me.[6]

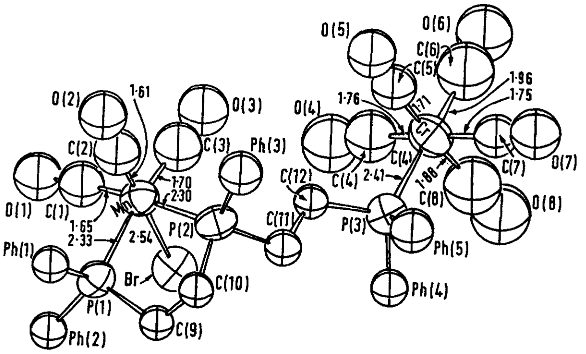

FIGURE. *Molecular structure of* (A). *E.s.d.s of bond lengths are:* Mn–Br, Mn–P, Cr–P, 0·01; Mn–C, Cr–C, 0·05 Å.

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