Journal of Organometallic Chemistry, 141 (1977) C10–C12

Preliminary Communication

THE CONTRASTING CO-ORDINATION BEHAVIOUR OF TETRAETHYL DIPHOSPHITE $(EtO)_2POP(OEt)_2$ AND 1,1,3,3-TETRAETHOXY-2-ETHYLDIPHOSPHAZANE $(EtO)_2PN(Et)P(OEt)_2$ AND RELATED COMPOUNDS*

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(Received September 19, 1977)

SUMMARY

In various metal carbonyl derivatives and platinum compounds, $(RO)_2PN(Et)P(OR)_2$ (R = Et or Ph) function as chelating bidentate ligands whereas $(EtO)_2POP(OEt)_2$ is monodentate or bridged bidentate.

While the co-ordination chemistry of tertiary phosphites, $P(OR)_3$ (R = alkyl or aryl group), and related ligands has been studied in considerable detail [1], that of ditertiary phosphites such as $(EtO)_2POP(OEt)_2$ has been little explored. This compound reacts with $Fe_2(CO)_9$ to give four products $[\{Fe(CO)_4\}_2\{(EtO)_2POP(OEt)_2\}]$, $[Fe_2(CO)_7\{(EtO)_2POP(OEt)_2\}]$, $[\{Fe(CO)_3\}_2\{(EtO)_2POP(OEt)_2\}_2]$, and $[Fe_2(CO)_5\{(EtO)_2POP(OEt)_2\}_2]$. The octa- and hexacarbonyl derivatives contain

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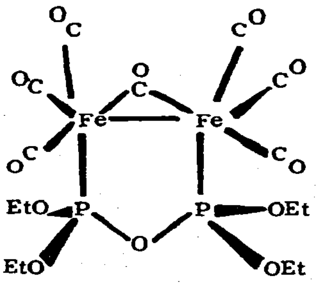
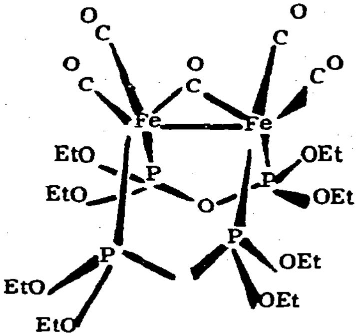
* No reprints available.

terminal carbonyls only, and are considered to be mono- and bis-substituted derivatives of $[Fe(CO)_5]$ with bridging bidentate $(EtO)_2POP(OEt)_2$. Terminal and bridging carbonyl groups are present in the hepta- and pentacarbonyl derivatives, and on the basis of this and other spectroscopic evidence structures I and II are proposed for these compounds. Structure I is analogous to that of $[Fe_2(CO)_7\{Ph_2PCH_2PPh_2\}]$ [2].


(I)


(II)

Compounds with $(EtO)_2POP(OEt)_2$ bridging were also isolated from reactions of $[Mo(\eta\text{-}C_5H_5)(CO)_3X]$ (X = Cl, Br or I) and $[Fe(\eta\text{-}C_5H_5)(CO)_2X]$ (X = Cl or I) with $(EtO)_2POP(OEt)_2$. These included $[\{Mo(\eta\text{-}C_5H_5)(CO)_2X\}_2\{(EtO)_2POP(OEt)_2\}]$ (three isomeric forms for X = I [3,4]), $[\{Fe(\eta\text{-}C_6H_5)(CO)I\}_2\{(EtO)_2POP(OEt)_2\}]$ and $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2\{(EtO)_2POP(OEt)_2\}][B(C_6H_5)_4]_2$. In contrast, from $[Mo(C_7H_8)(CO)_4]$ we obtained cis-$[Mo(CO)_4\{(EtO)_2POP(OEt)_2\}]$ in which the organic ligand is monodentate.

The reactions of palladium and platinum and compounds also failed to afford metal chelates. The compounds $[M_2Cl_4\{(EtO)_2POP(OEt)_2\}_2]$ (M = Pd, Pt) were obtained from $[PdCl_2(NCPh)_2]$ or $[PtCl_2(SEt_2)_2]$ and the i. r. and NMR data imply the presence of $(EtO)_2POP(OEt)_2$ bridges with phosphorus trans to chloride [5].

In contrast to $(EtO)_2POP(OEt)_2$, the compounds $(RO)_2PN(Et)P(OR)_2$ (R = Et or Ph) readily afforded chelated products on reaction with various metal carbonyls and platinum metal derivatives. For instance reaction of cis-$[PtCl_2(SEt_2)_2]$ and trans-$[PdCl_2(NCPh)_2]$ with these ligands gives cis-$[PtCl_2\{(RO)_2PN(Et)P(OR)_2\}]$ and cis-$[PdCl_2\{(EtO)_2PN(Et)P(OEt)_2\}]$ respectively. Significantly cis-$[PtCl_2\{(PhO)_2PN(Et)P(OPh)_2\}]$ is also obtained from the reaction of $[Pt_2Cl_4(PMe_2Ph)_2]$ with $(PhO)_2PN(Et)P(OPh)_2$ [5]. The reactions of $[M(C_7H_8)(CO)_4]$ (M = Cr, Mo or W) with

$(PhO)_2PN(Et)P(OPh)_2$ also provide examples of the formation of metal chelates with this ligand affording mononuclear $[M(CO)_4\{(PhO)_2PN(Et)P(OPh)_2\}]$.

The contrasting co-ordination properties of $(EtO)_2POP(OEt)_2$ and $(RO)_2PN(Et)$-$P(OR)_2$ (R = Et or Ph) can be related to differences in the POP and PNP bond angles. That for diphosphites is expected to be between 140 and 160^0 (cf. F_2POPF_2 with a POP bond angle of 150^0) [6], while that for PNP systems will be smaller. Formation of chelated structures therefore involves more strain for P–O–P compared with the P–N–P moeity.

ACKNOWLEDGEMENTS

We thank the South African Council for Scientific and Industrial Research and the Universities of Natal, Pretoria and Sussex for financial support.

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