Phosphorus-31 Hyperfine Coupling in Tetraphenylporphyrincobalt(II) Complexes of Trivalent Phosphorus Ligands and Dioxygen Complexes: Substituent Effects on the Phosphorus σ-Donor Orbital

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Summary Phosphorus-31 hyperfine splittings in tetraphenylporphyrincobalt(II) complexes with Et_3P and $(EtO)_3P$ and the corresponding dioxygen complexes are used in evaluating the influence of substituents on the nature of the phosphorus σ-donor orbital.

Tetraphenylporphyrincobalt(II) forms 1:1 complexes with trivalent phosphorus donors. E.s.r. spectra for these adducts indicate an axially symmetric g tensor and are only consistent with $(dxz,yz)^4(dxy)^2(dz^2)^1$ ground configuration (Figure and Table). The $g_{\parallel}$ and $g_{\perp}$ transitions are

TABLE. E.s.r. parameters and derived spin densities for Co^{II}(tpp) complexes of $P(Et)_3$ and $P(OEt)_3$

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}(^{59}Co)$ /cm^{-1} (G)	$A_{\perp}(^{59}Co)$ /cm^{-1} (G)	$a_{\parallel}(^{31}P)$ /cm^{-1} (G)	$a_{\perp}(^{31}P)$ /cm^{-1} (G)	$<a>^{31}P$ [a] /cm^{-1}	ρP_{3s} [b]	ρP_{3p} [b]	p/s [c]
$P(Et)_3$	2·02	2·24	0·0063 (67)	0·00285 (27)	0·02185 (232)	0·01757 (168)	0·01899	0·0559	0·1488	2·661
$P(OEt)_3$	2·02	2·24	0·0067 (71)	0·00293 (28)	0·02914 (308)	0·0268 (256)	0·02757	0·0811	0·0816	1·006

[a] $<a> = (a_{\parallel} + 2\,a_{\perp})/3$. [b] ρP_{3s} and ρP_{3p} are the spin densities in phosphorous 3s and 3p atomic orbitals.

$$\rho\,P_{3s} = \frac{a_{iso},}{a^{*}_{3s}},\ \rho P_{3p} = \frac{a_{\parallel} - a_{iso}}{a^{*}_{3p}}$$

$a^{*}_{3s} = 0·33963\ cm^{-1}(3640G)$ and $a^{*}_{3p} = 0·01922\ cm^{-1}(206G)$ are the atomic hyperfine coupling constants. [c] Ratio of p/s character in the phosphorus donor orbital.

split into two components by ^{31}P ($I = \frac{1}{2}$) hyperfine coupling and each of these components is further split into eight components by ^{59}Co ($I = 7/2$). Sigma bonding of the phosphorus ligands with Co(tpp) mixes the cobalt dz^2 with the ligand σ-donor orbital. This places spin density directly in the phosphorus σ-donor orbital which results in large ^{31}P hyperfine splitting. Phosphorus-31 coupling in the $g_{\parallel}$ region is substantially larger than in the $g_{\perp}$ region which is characteristic of an axially symmetric species with the g and ligand hyperfine tensors virtually coincident. Phosphorus 3s and 3p spin densities in the ligand σ-donor orbital are calculated from the observed coupling constants and the known atomic hyperfine values[1] (Table).

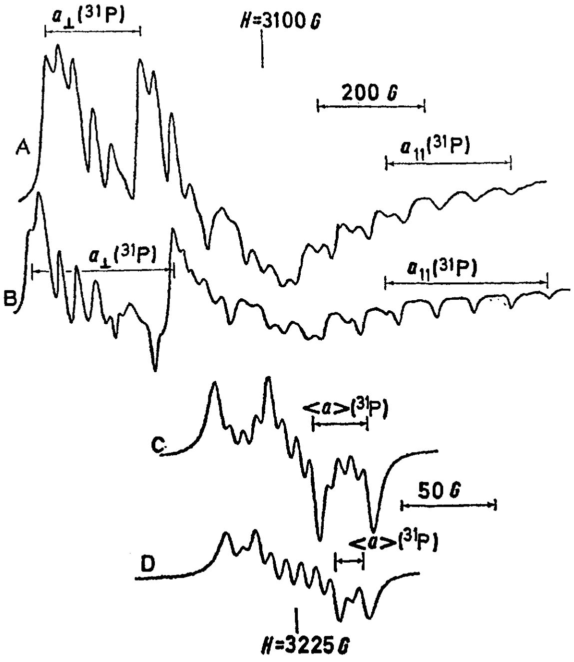

FIGURE. E.s.r. spectra for Co(tpp)L [L = Et_3P, $(EtO)_3P$] complexes in frozen toluene (−140 °C) and the corresponding dioxygen adducts in toluene solution (−60 °C). A: Co(tpp)PEt_3. B: Co(tpp)$P(OEt)_3$. C: Co(tpp)$P(OEt)_3 \cdot O_2$ $<g> = 2·023$, $<A\,^{59}Co> = 0·00067\ cm^{-1}$ (7·2G) $<a>^{31}P = 0·00271$ (28·8G). D: Co(tpp)P$(Et)_3 \cdot O_2$, $<g> = 2·023$ $<A\,^{59}Co> = 0·00074\ cm^{-1}$ (7·8G), $<a>$-$^{31}P = 0·00148$ (15·7G).

The experimentally determined fraction of phosphorus 3s character in the σ-donor orbitals of Et_3P and $(Et_3O)_3P$ of 0·27 and 0·50 show that the effective hybridization is very sensitive to the substituents. The more electronegative ethoxide substituent when compared to ethyl utilizes a larger fraction of the available 3p phosphorus orbitals in bonding and thus the σ-donor orbital for $(EtO)_3P$ has substantially larger phosphorus 3s character than Et_3P. SCF calculations[2] for $(Me)_3P$ and F_3P show the proper trends in donor orbitals P_{3s} character with substituent electronegativity, but may underestimate the actual value. The donor orbital s character for co-ordinated Et_3P (0·27) is substantially larger than the value found for the cation radical $[Et_3P]^+$ (0·10)[3] which probably reflects a large structural and electronic rearrangement accompanying ionisation. Introduction of spin density into the phosphorus ligand orbitals by co-ordination where the ligand structure is little affected represents a relatively small perturbation and provides a better description of the σ-donor orbital in the neutral ligand. The larger total phosphorus spin density for Et_3P (0·20) compared to $(EtO)_3P$ (0·16) probably reflects improved orbital overlap and energy matching with the cobalt dz^2 as the donor orbital p character increases (Table). The large substituent effects on the phosphorus donor orbital s and p character has wide implications in the interpretation of ^{31}P n.m.r. coupling constants,[4] metal–phosphorus bond distances,[5] and vibrational spectra[6] for metallo-phosphine complexes.

Complexes of Co(tpp) with Et_3P and $(EtO)_3P$ are found to form 1 : 1 dioxygen adducts. Phosphorus-31 hyperfine splitting is observed for these complexes and demonstrates that the phosphorus ligand remains co-ordinated in the oxygen adduct in solution and glass media (Figure). Previous e.s.r. studies of cobalt(II) dioxygen complexes have placed the odd electron in a predominantly oxygen π^* MO,[7] and the relatively small ^{31}P hyperfine splitting is consistent with this assignment.

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