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Preliminary communication

STRUCTURE/REACTIVITY RELATIONSHIPS FOR CATIONIC (PHOSPHENIUM)IRON TETRACARBONYL COMPLEXES

ALAN H. COWLEY*, RICHARD A. KEMP,
Department of Chemistry, University of Texas at Austin, Austin, TX 78712 (U.S.A.)
E.A.V. EBSWORTH*, DAVID W.H. RANKIN, and MALCOLM D. WALKINSHAW
Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ (Great Britain)
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Summary

An X-ray crystal structure of $[(Et_2N)_2PFe(CO)_4]^+$, reveals shortening of the P—Fe and $C—O_{eq}$ bonds and lengthening of the $Fe—C_{eq}$ bonds, possibly suggesting that the CO lability of cationic (phosphenium)iron tetracarbonyl complexes is due to the strong π-acceptor character of the phosphenium ligand.

Several cationic [1] and neutral [2] transition metal derivatives of two-coordinate phosphorus (phosphenium) cations have now been prepared. Interest in the ligand properties of phosphenium ions has been generated by the recognition that such species are isolobal with e.g. carbenes. An interesting study [3] of the reactivity of cationic (phosphenium)iron tetracarbonyl complexes has revealed that the R_2P^+ moiety is capable of labilizing the other ligands in the coordination sphere. In view of their emerging importance, it is perhaps surprising that different structures for $[(R_2N)_2PFe(CO)_4]^+$ complexes have been postulated on the basis of IR [1b,d] and Mössbauer [4] spectroscopic data. We undertook a single-crystal X-ray diffraction study of $[(Et_2N)_2PFe(CO)_4]^+[AlCl_4]^-$ (I) in order to (i) establish the solid-state structures of cationic (phosphenium)iron tetracarbonyl complexes, and (ii) determine whether structural evidence exists for the implied strong π-acceptor behavior for the phosphenium ligand.

The solid state of I features four crystallographically unrelated molecules per asymmetric unit.

Crystal data: $C_{12}H_{30}AlCl_4FeN_2O_4P$, M = 522.00, monoclinic, space group $P2_1/c$ (No. 14), a 17.547(8), b 29.007(20), c 17.876(5) Å, β 91.80(3)°, U 9094.1 Å^3, D_c 1.495 g cm^{-3}, Z = 16, λ(Mo-K_α) 0.71073 Å, μ(Mo-K_α) 12.7 cm^{-1}. An orange prismatic crystal (0.2 × 0.2 × 0.25 mm) was sealed under nitrogen in

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a Lindemann capillary, and data were collected at −108°C using an Enraf—Nonius CAD-4 diffractometer. 8742 unique reflections were measured to $2\theta_{max}$ of 40°. No crystal decay was observed and no absorption corrections were applied. All Fe and P positions of the four crystallograhpically-unrelated molecules were determined using direct methods [5] and refined using the SHELX program [6]. All non-hydrogen atoms were located from difference Fourier maps and refinement with Fe and P atoms with anisotropic thermal parameters converged to R = 0.08. Using a special procedure [7], it was possible to locate 70 of the 80 hydrogen atoms in the final refinement, giving final residuals of R = 0.055 and R_w = 0.058.

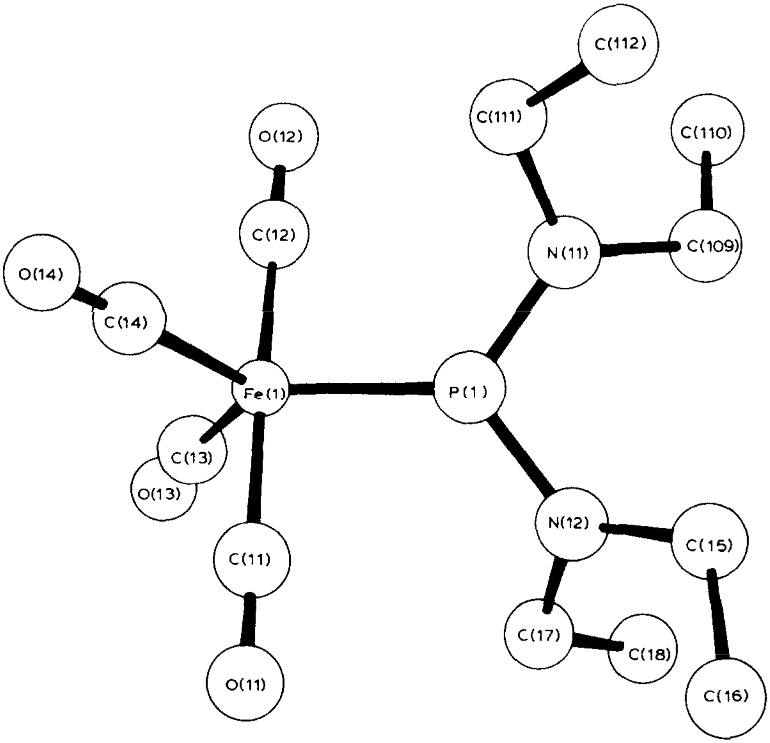

Fig. 1. View of one of four crystallographically-unrelated $[(Et_2N)_2PFe(CO)_4]^+$ cations showing the atom numbering scheme. Important (weighted mean) parameters: Fe(1)—P(1) 2.10(5), Fe(1)—C(11) 1.80(2), Fe(1)—C(12) 1.76(4), Fe(1)—C(13) 1.81(1), Fe(1)—C(14) 1.83(4), P(1)—N(11) 1.61(3), P(1)—N(12) 1.62(1) Å, C(11)—Fe(1)—C(12) 178(1), C(13)—Fe(1)—C(14) 114(3), N(11)—P(1)—N(12) 106(3)°.

All four crystallographically independent cations exhibit similar geometries (Fig. 1). In each cation the phosphenium ligand adopts an equatorial site of a local trigonal bipyramidal iron geometry, and an approximate C_2 axis exists along the Fe—P bond. This is an unusual result in the sense that all (phosphine)-iron tetracarbonyl complexes [8] except $(Ph_2P)_2(Ph)PFe(CO)_4$ [9] feature the phosphorus ligand in an axial position. Equatorial substitution in the case of I appears to be a consequence of the π-acceptor nature of the phosphenium ligand. Thus, the geometry at phosphorus is planar and the average Fe—P bond length of 2.10(5) Å is among the shortest such distances for phosphorus-substituted iron tetracarbonyl complexes. Furthermore, theoretical modelling by Rossi and

Hoffmann [10] has demonstrated that for d^8—d^{10} trigonal bipyramidal systems a π-acceptor ligand prefers an equatorial location with the vacant *np* orbital in the equatorial plane. However, in I the N—P—N plane is tilted between 31 and 38° from the plane passing through Fe—P—CO_{ax}, coplanarity being precluded by the non-bonded contacts between the CH_2 groups and CO_{ax} carbon atoms.

The observed CO lability of cationic (phosphenium)iron tetracarbonyl complexes can be attributed to the strong π-acceptor character of the R_2P^+ ligand [3]. The present observation that the Fe—C_{eq} bonds (1.82(5) Å) are longer than the Fe—C_{ax} bonds (1.78(5) Å) is consistent with this view since this is the reverse of the trend observed for axially-substituted $\geqslant PFe(CO)_4$ complexes [8]. However, note that the difference in these bond lengths is not very significant. Moreover, as noted by Bennett and Parry [3], the structure of the transition state may be as important as that of the ground state when considering lability.

Finally, we note that the metric parameters for the coordinated $[(Et_2N)_2P]^+$ ligand are very similar to those for the uncoordinated isopropyl analogue [11] the only significant change upon coordination being narrowing of the N—P—N angle by approximately 10°.

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