Crystal and Molecular Structures of Hexafluoroacetone and Hexafluoroisopropylideneamine Complexes of Nickel

By RACHEL COUNTRYMAN and B. R. PENFOLD*

(*Department of Chemistry, University of Canterbury, Christchurch, New Zealand*)

Summary Crystal structure determinations on $(Ph_3P)_2\overline{Ni{\cdot}C(CF_3)_2O}$ and $(Bu^tNC)_2\overline{Ni{\cdot}C(CF_3)_2NH{\cdot}C(CF_3)_2O}$ have established the geometries of two classes of compounds formed by co-ordination of fluorocarbon molecules to transition metals; in the first case a symmetrical three-membered ring is formed by co-ordination of one molecule of $(CF_3)_2CO$ and in the second case a five-membered ring is formed by co-ordination of one molecule of $(CF_3)_2CO$ and one molecule of $(CF_3)_2CNH$.

THE nickel complex $(PPh_3)_2\overline{Ni{\cdot}C(CF_3)_2O}$ is one of a number of related compounds in which one molecule of hexafluoroacetone is co-ordinated to Ni or Pt.[1] We have taken it as a model compound for a study of the precise manner of this co-ordination; it was prepared either by ligand exchange from $\pi\text{-}C_8H_{12}\overline{Ni{\cdot}C(CF_3)_2O}$[2] or by reaction of $(PPh_3)_2Ni(C_2H_4)$ with hexafluoroacetone in ether.[3]

The deep orange crystals of $(PPh_3)_2\overline{Ni{\cdot}C(CF_3)_2O}$ are monoclinic (space group $P2_1/n$) with $a = 18{\cdot}123$, $b = 19{\cdot}879$, $c = 9{\cdot}745$ Å; $\beta = 93{\cdot}46°$; $U = 3504$ Å^3; $Z = 4$; $D_m = 1{\cdot}48(2)$; $D_c = 1{\cdot}43$ g cm^{-3}. The crystals are sensitive to air and X-rays. 1406 independent reflections were used in the crystal structure determination by conventional heavy-atom methods. In the final least-squares refinement the phenyl rings were treated as rigid regular hexagons while the nickel and fluorine atoms alone were treated anisotropically. The conventional R-factor is 0·087.

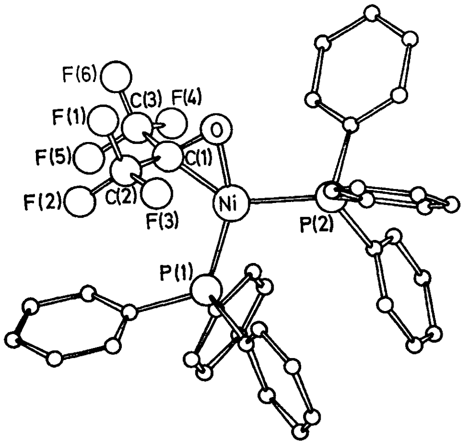

FIGURE 1. *A general view of one molecule of* $(Ph_3P)_2\overline{Ni{\cdot}C(CF_3)_2O}$.

The structure is illustrated in Figure 1 which shows that the carbonyl group is symmetrically bonded sideways on to nickel. Relevant bond lengths are: Ni–P, 2·18(1) and 2·25(1); Ni–O, 1·87(1); Ni–C(1), 1·89(2); C(1)–O, 1·32(2) Å. The angle at Ni in the three-membered ring is 41·3(6)°. In this first authenticated structure containing a sideways co-ordinated carbonyl group, the C=O bond has been significantly lengthened by 0·09(2) Å relative to the bond in the free molecule. The planar geometry of the co-ordination sphere is distorted so that the plane containing nickel and the co-ordinated carbonyl group is tilted significantly, by 6·9°, with respect to that defined by the nickel and phosphorus atoms.

Treatment of the analogous complex, $(Bu^tNC)_2Ni{\cdot}C(CF_3)_2O$ with $(CF_3)_2CNH$ affords a single isomer of $(Bu^tNC)_2\overline{Ni{\cdot}C(CF_3)_2NH{\cdot}C(CF_3)_2O}$.[4] The yellow crystals are monoclinic (space group $P2_1/c$) with $a = 10{\cdot}497$, $b = 17{\cdot}870$, $c = 12{\cdot}717$ Å; $\beta = 104{\cdot}6°$; $U = 2308$ Å^3; $Z = 4$; $D_m = 1{\cdot}61(2)$, $D_c = 1{\cdot}60$ g cm^{-3}. The structure was solved by conventional heavy-atom methods using 978 independent reflections. Nickel and fluorine atoms were treated anisotropically in the final stages of the least-squares refinement. The R-factor is 0·066. (For both of the structure analyses reported here, X-ray intensity data were recorded with a Hilger–Watts four-circle diffractometer using Zr-filtered Mo-K_α radiation and the moving-crystal–moving-counter scan technique, backgrounds being measured with crystal and counter stationary.)

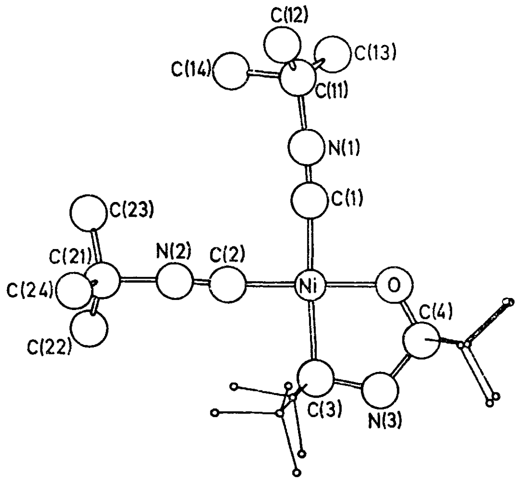

FIGURE 2. *A general view of one molecule of* $(Bu^tNC)_2\overline{Ni{\cdot}C(CF_3)_2NH{\cdot}C(CF_3)_2O}$.

The structure is illustrated in Figure 2, CF_3 groups being shown schematically for clarity. The oxygen and nitrogen atoms in the five-membered ring were positively identified by observing the behaviour of their temperature factors under least-squares refinement when the two atoms were interchanged. [Final values for the isotropic thermal parameters for oxygen and nitrogen were 4·8(3) and 3·9(3) Å^2 respectively while interchanging these atoms gave values of 2·1(2) and 6·6(3) Å^2 respectively.] Bond lengths in the nickel co-ordination sphere and in the five-membered ring are: Ni–O, 1·81(1); Ni–C(3), 2·00(2); Ni–C(1), 1·83(2);

Ni–C(2), 1·77(2); O–C(4), 1·35(2); N(3)–C(4), 1·40(2); N(3)–C(3), 1·42(2) Å. The angle at Ni in the five-membered ring is 86·5(6)°. There are small but significant (up to 0·08 Å) departures from planarity in the five-membered ring but the mean plane of this ring is not twisted significantly from the plane of Ni, C(1), and C(2).

Of great significance is the fact that the oxygen atom of the ring rather than the nitrogen is bonded to the nickel. This establishes that in the formation of the compound, the imine has been inserted into the Ni–C bond of $\mathrm{(Bu^tNC)_2}$-$\overline{\mathrm{Ni{\cdot}C(CF_3)_2O}}$, the Ni–O bond remaining unbroken. This result has led Stone[1] to favour a mechanism involving a six-co-ordinate intermediate in which both fluorocarbon molecules are bonded to the nickel in preference to a mechanism involving a dipolar intermediate. Thus the most probable dipolar intermediate $\mathrm{(Bu^tNC)_2Ni^{+}{\cdot}C(CF_3)_2O^{-}}$ would be expected to lead not to the isomer which we have established but to the alternative isomer in which nitrogen rather than oxygen is bonded to nickel.

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