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New Routes to Fluorocarbon Nickel Complexes

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Treatment of tetrakistriphenylphosphine–palladium or –platinum with certain fluorocarbon compounds has led to the synthesis of a variety of complexes, for example $(Ph_3P)_2Pd[(CF_3)_2CO]$ [1] or $(Ph_3P)_2Pt[C_2F_4]$.[2] We have now found that bis(cyclo-octadiene)nickel[3] and allylnickel compounds such as bis(methallyl)nickel[4] are highly reactive towards fluorocarbons, forming fluoro-organonickel complexes of a new type.

Bis-(2-methallyl)nickel reacts rapidly with tetrafluoroethylene forming a deep red crystalline complex, $C_{12}H_{14}F_8Ni$ (I), m.p. 110—111°. The ^1H and ^{19}F n.m.r. spectra are in accord with the structure proposed, with proton signals at τ 4·95 (2H, d, $J_{HH} < 0·5$ c./sec.), 5·17 (2H, d, $J_{HH} < 0·5$ c./sec.), 7·22 (4H, t, J_{HF} 18·0 c./sec.), and 8·01 (6H, s); and fluorine resonances (relative to CCl_3F) at 100·7 (4F, s) and 107·9 (4F, t, J_{HF} 18·0 c./sec.).

Formation of a tetrafluoroethylene complex is of interest in itself, but the concomitant insertion of a second tetrafluoroethylene molecule between two π-methallyl groups to form the 4,4,5,5-tetrafluoro-2,7-dimethylocta-1,7-diene system is without precedent. Treatment of (I) with iodine affords $CH_2{:}CMe{\cdot}CH_2(CF_2)_2CMe{\cdot}CH{:}CH_2$.

Bis(cyclo-octa-1,5-diene)nickel reacts with hexafluoroacetone and 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietan below 0° to afford, respectively, the orange crystalline complexes (II), decomp. > 82° and (III), m.p. 165·5°. Treatment of (II) or (III) with the ligands Ph_2PMe, Ph_3P, $(PhO)_3P$, $EtC(CH_2O)_3P$, $[Ph_2PCH_2]_2$, or dipyridyl results in displacement of cyclo-octa-1,5-diene and the formation in high yield of the stable crystalline complexes (IV) and (V) respectively. The complex (IV; L = Ph_2PMe) can also be prepared by treating tetrakis(methyldiphenylphosphine)nickel with hexafluoroacetone.

Analytical and molecular weight data, infrared and n.m.r. spectra, and degradation studies are all in accord with the structures proposed for complexes (II)—(V). In its infrared spectrum, hexafluoroacetone shows a strong carbonyl stretching band[5] at 1807 cm.$^{-1}$. No such band is present in the spectra of complexes (II) or (IV), nor are there bands assignable to either the arrangement $(CF_3)_2C{=}O{\rightarrow}Ni$ or to a π-complex of hexafluoroacetone and nickel. Moreover, the absence of terminal metal carbonyl bands or acyl carbonyl bands excludes structures [*e.g.* $(CF_3)_2NiL_2(CO)$ or $CF_3CONiL_2(CF_3)$] in which hexafluoroacetone has become fragmented on co-ordination. The possibility is further disproved by chemical properties and ^{19}F n.m.r. studies. Treatment of (II) with carbon monoxide afforded tetracarbonylnickel, cyclo-octa-1,5-diene, and hexafluoroacetone. The ^{19}F spectra of (II) and (III) show sharp singlets at 68·1 and 57·9 p.p.m. respectively, relative to CCl_3F. The chemical shift of a CF_3 group directly attached to nickel is about $-6·0$ p.p.m.[6] in accord with the generally observed low-field shifts of fluorine nuclei on carbon atoms σ-bonded to transition metals.[7] Moreover, the n.m.r. data for (IV) and (V) are also in accord with a rigid three-membered ring system in that two phosphorus–fluorine coupling constants are observed. The ^{19}F n.m.r. spectrum of [IV; L = $(PhO)_3P$], m.p. 130—131°,[5] shows a band at 66·5 p.p.m. (double-doublet, $J_{cis\text{-}PF}$ 3·4, $J_{trans\text{-}PF}$

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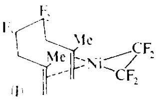
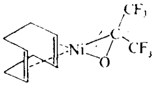
12·2 c./sec.); and similarly the spectrum of [V; L = $(PhO)_3P$], m.p. 133°, has a band at 56·5 p.p.m. (double-doublet, $J_{cis\text{-}PF}$ 1·0, $J_{trans\text{-}PF}$ 12·0 c./sec.). The stability of the triangular NiCO and NiCS structures in hexafluoroacetone and hexafluorothioacetone complexes is interesting, and is demonstrated by the formation of (IV) and (V) from (II) and (III), respectively. The bonding for attachment of the $(CF_3)_2CO$ or the $(CF_3)_2S$ groups to nickel could be rationalized in terms of a three-centre molecular orbital scheme.[8]


(I)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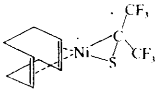
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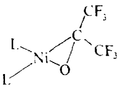
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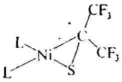
(V)

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