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Reactions of Low-valent Metal Complexes with Fluorocarbons. Part XVIII¹ t-Butyl Isocyanide–Nickel Complexes

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Reaction of Ni(Bu^tNC)₄ with (CF₃)₂CO and with (CF₃)₂CNH affords (Bu^tNC)₂NiC(CF₃)₂·X·C(CF₃)₂·X (X = O or NH). The same five-membered ring compounds are obtained by treating $(Bu^{t}NC)_{2}NiC(CF_{3})_{2}\cdot X$ (X = 0 or NH). prepared from $(1,5-C_8H_{12})NiC(CF_3)_2\cdot X$, with the respective ketone or imine. Whereas, treatment of $(Bu^tNC)_2$ - $NiC(CF_3)_2 O$ with $(CF_3)_2CNH$ gives only $(Bu^tNC)_2NiC(CF_3)_2 NH \cdot C(CF_3)_2 O$, the reaction of $(Bu^tNC)_2 - C$ I NiC(CF₃)₂·NH with (CF₃)₂CO affords a <u>mixture of</u> two five-membered ring complexes. Hexafluoroacetone reacts with Ni(PhNC)₄ to form (PhNC)₂NiC(CF₃)₂·O, which reacts further with hexafluoroisopropylideneamine to give $(PhNC)_2^{I}NiC(CF_3)_2 NH C(CF_3)_2 O$. Tetrafluoroethylene and hexafluorobuta-1,3-diene react with Ni(Bu^tNC)₄ to form, respectively $(Bu^tNC)_2$ -

NICF₂·CF₂·CF₂·CF₂ and (Bu^tNC)₂NICF₂·CF:CF·CF₂, whereas the corresponding reaction with (CN)₂C:C(CF₃)₂ or CF_3CF_2 give, respectively, $(Bu^tNC)_2NiC(CF_3)_2 \cdot C(CN)_2$ and $(Bu^tNC)_2NiCF_2 \cdot CFCF_3$.

Treatment of $(Bu^tNC)_2Ni(O_2)$ with hexafluoroacetone gives $(Bu^tNC)_2NiO\cdotO\cdot C(CF_3)_2\cdot O$, which forms a 1:1 adduct with (CF₃)₂CO, and readily transfer oxygen to diethyl ether forming (Bu^tNC)₂NiO·C(CF₃)₂·O

PREVIOUS studies 1-3 of the reaction of fluoro-olefins, -ketones, and -imines with low-valent transition-metal complexes indicated that co-ordination of one molecule of substrate could lead to an apparent activation of these unsaturated systems towards reaction with a second electronegatively substituted unsaturated molecule. Whereas tetrafluoroethylene reacts with $Pt(PPh_3)_A$ to form $(Ph_3P)_2PtCF_2 \cdot CF_2$,⁴ the corresponding re-action with a zerovalent nickel complex gave L_2 NiCF₂·CF₂·CF₂·CF₂ (L = tertiary-phosphine, -phosphite,² or -arsine¹), implying that in the complexes L_2 NiCF₂·CF₂ ⁵ the co-ordinated tetrafluoroethylene molecule is activated towards further reaction with C_2F_4 . A related observation³ is that the hexafluoroisopropylideneamine complex (Ph₃P)₂PtC(CF₃)₂·NH re-¹ Part XVII, Jane Browning, M. Green, and F. G. A. Stone,

acts with hexafluoroacetone to form a compound which is either $(Ph_3P)_2PtC(CF_3)_2\cdot NH\cdot C(CF_3)_2\cdot O$ or its isomer $(Ph_3P)_2PtC(CF_3)_2 \cdot O \cdot C(CF_3)_2 \cdot NH$. Moreover, NiL_4 [L₂ = 1,2-(Me₂As)₂C₆H₄] reacts with hexafluoroacetone or hexafluoroisopropylideneamine to form $L_2 \dot{NiC}(CF_3)_2 \cdot X \cdot C(CF_3)_2 \cdot \dot{X} (X = O \text{ or } NH, respectively}).^1$ These observations suggest activation of co-ordinated $(CF_3)_2C=X$ (X = O or NH). It is clear that both the metal and the co-ordinated ligands can have an effect on the extent of ' activation,' and with a view to understanding these reactions more fully we have investigated 3- to 5-membered ring-expansion reactions with isocyanide-nickel complexes. The new compounds obtained were characterised by elemental analysis, i.r.

J. Chem. Soc. (A), 1971, 453.
 ² C. S. Cundy, M. Green, and F. G. A. Stone, J. Chem. Soc. (A), 1970, 1647.

³ J. Ashley-Smith, M. Green, and F. G. A. Stone, J. Chem.

J. Asiney-Siniti, M. Green, and P. G. A. Stone, J. Chem.
 M. Green, A. J. Rest, R. B. L. Osborn, and F. G. A. Stone, J. Chem. Soc. (A), 1968, 2525.
 A. Greeo, M. Green, S. K. Shakshooki, and F. G. A. Stone, Chem. Comm. 1070, 1374.

Chem. Comm., 1970, 1374.

spectroscopy, and ¹H and ¹⁹F n.m.r. spectroscopy. The observation of two $\nu_{\rm NC}$ stretching bands of equal intensity in the spectra of all the compounds described establishes a relative *cis*-configuration for the isocyanide ligands.⁶

An excess of hexafluoro-acetone or -isopropylideneamine reacts at room temperature with an ether solution require cleavage of the carbon-oxygen or -nitrogen bonds of $(CF_3)_2CX$ (X = O or NH), and such a process seems unlikely.

Tetrafluoroethylene and hexafluorobuta-1,3-diene both react at room temperature with tetrakis-(t-butylisocyanide)nickel to form, respectively, octafluoronickelacyclopentane (III) and hexafluoronickelacyclopent-3-



of tetrakis-(t-butylisocyanide)nickel⁶ to form respectively (in high yield) the yellow crystalline complexes (I) and (II); formulated as 5-membered ring compounds, in which the two hexafluoroacetone or hexafluoroisopropylideneamine molecules are linked head to tail, *i.e.* structures (Ia) and (IIa). This form of linkage is favoured over the alternative head-to-head structures (Ib), (Ic), (IIb), and (IIc), because the ¹⁹F n.m.r. spectra show two multiplets of equal intensity with chemical shifts separated by some 16 p.p.m., and it seems unlikely that even with a puckered head-to-head structure such widely different shifts would be observed. Moreover, in the case of the related platinum compound, referred to above, similar widely separated chemical shifts were observed with only the low-field multiplet showing ¹⁹⁵Pt-¹⁹F coupling. This supports the assignment of the high-field shift in (I) and (II) to a $C(CF_3)_2$ group remote from the metal. The further alternative structures (Id) and (IId) were rejected because their formation would

ene (IV) compounds, isostructural with previously reported complexes $L_2NiCF_2 \cdot CF_2 \cdot CF_2$ (L = phosphine,² phosphite,² arsine¹) and $L_2NiCF_2 \cdot CF \cdot CF_2$ [L = PhAsMe₂, or $L_2 = 1,2 \cdot (Me_2As)_2C_6H_4$ ¹]. Thus the ¹⁹F n.m.r. spectrum of (III) showed bands of equal intensity (rel. CCl₃F) at 101.6 and 138.2 p.p.m., which may be compared with those in the spectrum of (Ph₂PMe)₂-NiCF₂ · CF₂ · CF₂ · CF₂ at 101.5 and 138.8 p.p.m.² The ¹⁹F spectrum of (IV) with multiplet resonances at 87.5 and 147.7 p.p.m., relative intensity 2 : 1, is very similar to that of (Me₂PhAs)₂NiCF₂ · CF:CFCF₂ [84.9 (4F) and 148.6 (2F)]. In addition, the i.r. spectrum of (IV) showed a band at 1750 cm.⁻¹, which is assigned to the CF₂CF:CFCF₂ stretching frequency.

Whereas, in the reactions described above the only products are 5-membered ring compounds, reaction between tetrakis(t-butylisocyanide)nickel with an excess of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene affords

⁶ S. Otsuka, A. Nakamura, and Y. Tatsuno, J. Amer. Chem. Soc., 1969, **91**, 6994.

the crystalline complex (V); which because of the high ⁶ v_{NC} stretching frequencies and for reasons previously discussed,^{2,4,7} is depicted as being formally a 3-membered ring Ni^{II} complex. A similar change in reaction type is observed when one of the fluorine atoms in tetrafluoroethylene is replaced by a trifluoromethyl group; hexafluoropropene reacts with Ni(ButNC)4 to give very unstable crystals of (VI), which is apparently an analogue of the previously described 3-membered ring compounds

 $\dot{N}iC(CF_{a})_{a}\dot{N}Me$ has also been obtained.

In contrast with the formation of (Ia) from Ni(Bu^tNC)₄, tetrakis(phenylisocyanide)nickel reacts with hexafluoroacetone to give the 3-membered ring complex (VIII), the ¹⁹F n.m.r. spectrum of which shows a resonance at 67.7 p.p.m., characteristic of complexes of this type.⁸ The identity of (VIII) was confirmed by an alternative synthesis. Reaction of (1,5-C₈H₁₂)NiC(CF₃)₂·O with two

molar equivalents of phenyl isocyanide leads to the displacement of cyclo-octa-1,5-diene and the formation of (VIII). The inability of the latter complex to react with an excess of hexafluoroacetone in diethyl ether to form a 5-membered ring complex similar to (Ia) may be related to withdrawal by the phenyl isocyanide ligands of electron density from the nickel by π -bonding so that the nucleophilicity of the metal is reduced. However, treatment of (VIII) with hexafluoroacetone in benzene as solvent gave a material the ¹⁹F n.m.r. of which showed peaks at 67.7 and 82.0 p.p.m., but of relative intensity 20:1 suggesting that ring expansion had occurred to a small degree. Only (VIII) could be recovered, however, from the reaction mixture.

In order to test whether the 5-membered ring compounds (I) and (II) are formed via 3-membered ring intermediates which rapidly react with a further molecule of $(CF_3)_2CX$ (X = O or NH), the crystalline complexes (IX) (Bu^tNC)₂NiC(CF₃)₂·O and (X) (Bu^tNC)₂- $\operatorname{NiC}(\operatorname{CF}_3)_2$, NH were synthesised by the displacement of cyclo-octa-1,5-diene from $(1,5-C_8H_{12})$ NiC(CF₃)₂·X (X = O⁸ or NH³) by t-butyl isocyanide. Reaction of (IX) with an excess of hexafluoroacetone or (X) with hexafluoroisopropylideneamine in diethyl ether at room temperature gave respectively (Ia) and (IIa) identical with the complexes obtained directly from tetrakis(tbutylisocyanide)nickel.

Both (IX) and (X) also react with tetrafluoroethylene, but to give the octafluoronickelacyclopentane complex

(III), rather than the 5-membered ring compounds $(Bu^{t}NC)_{2}\dot{N}iC(CF_{3})_{2}\cdot X\cdot CF_{2}\cdot CF_{2}$. This suggests that $(CF_3)_2CX$ (X = O or NH) is displaced by C_2F_4 from (IX) or (X) to give the reactive 3-membered ring complex $(Bu^{t}NC)_{2}\dot{N}iCF_{2}\dot{C}F_{2}$, which reacts with tetrafluoroethylene to give (III). There is precedent for such an exchange reaction, in that treatment of (Ph₃P)₂- $PtC(CF_3)_2$ ·NH with tetrafluoroethylene gives $(Ph_3P)_2$ -PtCF, CF, 9

Treatment of (IX) with hexafluoroisopropylideneamine leads to a 3- to 5-membered ring expansion reaction and the formation of only one of the possible





isomeric 5-membered ring compounds, which is considered to have either structure (XIa) or (XIb).* In contrast, hexafluoroacetone reacts with (X) to give both (XIa) and (XIb); the predominant isomer is that obtained from the reaction of (IX) with hexafluoroisopropylideneamine.

Although as described above there is little evidence

for a reaction of (VIII) (PhNC)₂NiC(CF₃)₂O with hexafluoroacetone, treatment of (VIII) with hexafluoroisopropylideneamine affords the 5-membered ring compound (XII), which can have either of the two possible structures (XIIa) or (XIIb), of which the latter seems more likely.*

These results have firmly established a reaction path to 5-membered ring fluorocarbon-nickel compounds via 3-membered ring complexes. The recent reports 10,11

that the peroxo-platinum complex (Ph₃P)₂PtO[•]O reacts

⁸ Jane Browning, C. S. Cundy, M. Green, and F. G. A. Stone, J. Chem. Soc. (A), 1969, 20.
⁹ J. A. Smith, Ph.D. Thesis, Bristol University, 1970.
¹⁰ R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, Change County, 1969, 1469.

^{*} Added in proof: A single crystal X-ray diffraction study (B. R. Penfold and R. M. Countryman, personal communication) has established structure (XIb) with a nearly planar 5-membered ring, *i.e.* ring expansion of (IX) involves opening of the carbonnickel bond.

⁷ R. Burt, M. Cooke, and M. Green, J. Chem. Soc. (A), 1970, 2975.

Chem. Comm., 1968, 1498.

¹¹ P. J. Hayward, D. M. Blake, C. J. Nyman, and G. Wilkinson, J. Amer. Chem. Soc., 1970, 92, 5873.

with CO_2 , CS_2 , aldehydes and ketones to give 5-membered ring compounds, the identity of the acetone adduct $(Ph_3P)_2PtO\cdot O\cdot C(CH_3)_2 \cdot O$ having been established ¹⁰ by X-ray crystallography, suggested an investigation of the

reaction of (Bu^tNC)₂NiO·O ⁶ with hexafluoroacetone.

Hexafluoroacetone (one molar equivalent) reacts with (peroxo)bis(t-butylisocyanide)nickel in diethyl ether at -50° to form a crystalline 1 : 1 adduct (XIII), which was difficult to analyse on account of its explosive decomposition when heated but which on the basis of a single ¹⁹F n.m.r. resonance at 82.6 p.p.m. is assigned the illustrated peroxo-structure in which the C(CF₃)₂ group occupies a β -position relative to the metal.

Treatment of (XIII) or (Bu^tNC)₂NiO·O with an excess of hexafluoroacetone gives yellow crystals of (XIV); this is a rather labile compound which reversibly loses one molecular equivalent of hexafluoroacetone. The ¹⁹F n.m.r. spectrum showed two singlet resonances of equal intensity at 82.5 and 83.5 p.p.m. indicating the presence of two $C(CF_3)_2$ groups in different environments such that ¹⁹F-¹⁹F coupling does not occur. It is tentatively suggested that the 5-membered ring system present in (XIII) is retained on formation of (XIV) and that the second molecule of hexafluoroacetone is loosely bonded to the nickel through oxygen so that the ¹⁹F chemical shift is at a relatively high field. This is supported by the presence in the i.r. spectrum of (XIV) of a band at 1670s cm.⁻¹, corresponding to v_{CO} of hexafluoroacetone [unco-ordinated the band is at 1810s cm.⁻¹ (gas phase)]. It is difficult to rationalise the appearance of such a band in the i.r. spectrum, if the reversible reaction (XIII) \implies (XIV) involves a 5- to 7-membered ring expansion; moreover, such a reaction seems unlikely because it would involve the facile making and breaking of a nickel-oxygen σ-bond.

The compound (XIII) is unstable in diethyl ether, one of the peroxy-oxygen atoms transferring to the solvent. The crystalline product (XV) of the oxygen-transfer reaction showed a singlet ¹⁹F n.m.r. resonance at **79**·9 p.p.m., and examination of the i.r. spectrum of (XV) revealed the absence of a band at 900m cm.⁻¹ assignable ⁶ to an O-O stretch, which is present in (XIII). It is suggested that (XV) has the illustrated four-membered ring structure. Interestingly, C_2F_4 reacts with (Bu^{*}NC)₂-

NiO·O with displacement of oxygen and formation of (III).

We have previously suggested that the 3- to 5membered ring expansion reactions involve octahedral intermediates, which can either rearrange within the co-ordination sphere to form the ring expanded products or lead to an exchange or displacement reaction. Moreover, since ionic intermediates have been implicated ¹² in the formation of complexes of the type described in this paper it seems probable that any octahedral transition state would involve polarised substrate molecules.

As mentioned above, the inability of (VIII) to ring expand with more hexafluoroacetone, whereas (IX) does so readily, can be explained in terms of the relative donor properties of PhNC and Bu^tNC influencing the oxidative ability of nickel, which in the extreme case (see Scheme) would formally involve conversion of nickel(II) to nickel(IV). However, such a complete change in oxidation state may not be necessary. Co-ordination of a second molecule of fluorocarbon substrate might be accompanied by a simultaneous withdrawal of metal electrons from the anti-bonding orbitals of the ligands already present, so that in the transition state the oxidation state of the metal might not be far removed from +2. The observation that (XII) forms on treatment of (VIII) with hexafluoroisopropylideneamine further emphasises 3 the role of the substrate in ringexpansion reactions; the ability to donate and accept electrons is crucial to the formation of an intermediate.

The lack of stereospecificity observed on reaction of (X) with $(CF_3)_2C:O$, whereas (IX) reacts with $(CF_3)_2C:NH$ to give (XIb), suggests that the postulated octahedral intermediate has a long enough lifetime to allow free rotation of the co-ordinated hexafluoro-acetone or -iso-propylideneamine.



It is then necessary to assume that one of the intermediates collapses to a 5-membered ring compound faster than rotation.

An alternative explanation, which does not require the assumption of free rotation, is that the intermediate from the reaction of (X) with $(CF_3)_2CO$ collapses to give (IX) faster than forming (XIa); the 3-membered ring complex (IX) then reacts with the displaced $(CF_3)_2C$:NH to form (XIb). However, this seems unlikely because in the reaction an excess of hexafluoroacetone is used, and therefore if (IX) was formed this would react with (((CF_3)_2COI to form appreciable amounts of (I), for which there was no evidence.

It has been suggested ¹⁰ that the addition of ketones, aldehydes, *etc.* to the complex $(Ph_3P)_2PtO\cdot O$ to form

¹² J. A. Smith, M. Green, and D. C. Wood, J. Chem. Soc. (A), 1970, 1848.

5-membered ring peroxo-complexes involves direct nucleophilic attack by the co-ordinated oxygen on the organic carbonyl group; the co-ordinated oxygen molecule is considered to be in the ${}^{3}\Sigma\bar{u}$ excited state, *i.e.* polarised as O⁺-O⁻. Such a reaction does not necessarily require co-ordination of the reacting carbonyl compound. However, although co-ordinated C₂F₄, (CF₃)₂C:O, and (CF₃)₂C:NH may be similarly polarised, thus providing a ready explanation for the head-to-tail linkage observed in the 5-membered ring compounds (I) and (II) and elsewhere, ^{1,3} the observed exchange reactions

including the report 6 that $({\rm Bu^tNC})_2 {\rm \dot{N}iO}{\rm \cdot\dot{O}}$ reacts with

 $(CN)_2C:C(CN)_2$ to form $(Bu^tNC)_2NiC(CN)_2 \cdot C(CN)_2$, almost certainly do require co-ordination of the reacting electronegatively substituted unsaturated molecule. We suggest therefore, that the formation of (XIII) from

 $(Bu^{t}NC)_{2}\dot{N}iO\cdot\dot{O}$ and $(CF_{3})_{2}C\cdot O$ proceeds *via* an analogous reaction path to that postulated in the formation of, for example, (I), (II), (III), and (XI).

EXPERIMENTAL

¹H and ¹⁹F N.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 and 94·1 MHz respectively. Chemical shifts are relative to Me₄Si (τ 10·00) and CCl₃F (0·00 p.p.m. external standard). I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer using Nujol and hexachlorobutadiene mulls.

Reactions of Tetrakis-(t-butylisocyanide)nickel.-(a) With hexafluoroacetone. An excess of hexafluoroacetone (0.42 g., 2.5 mmoles) was condensed (-196°) into a Carius tube containing tetrakis-(t-butylisocyanide)nickel⁶ (0.50 g., 1.2 mmoles) dissolved in diethyl ether (30 ml.). After 48 hr. at room temperature, the yellow solution was filtered, and reduced in volume (5 ml.). Addition of light petroleum (10 ml.) and cooling to -78° gave yellow crystals of (I) (0.47 g., 70%), m.p. 160° (Found: C, 34.9; H, 3.6; F, 40.6; N, 4.8. C₁₆H₁₈F₁₂N₂NiO₂ requires C, 34.5; H, 3.2; F, 40.9; N, 5.0%), ν_{max} 2238vs (ν_{NC}), 2220vs (ν_{NC}), 1300vw, 1238w, 1263w, 1230w, 1205m, 1190m, 1150w, 1015w, 1077m, 1040w, 970m, 940m, 926vw, 850vw, 800vw, 755vw, 730w, 723m, 710m, and 700vw cm.⁻¹. The ¹H n.m.r. spectrum (CDCl₃) showed a single resonance at $\tau 8.7$ (s,* 18H, Bu^t). The ¹⁹F n.m.r. spectrum (Et₂O) showed resonances at 64.3 [m, 6F, α -C(CF₃)₂] and 80.7 p.p.m. [m, 6F, β -C(CF₃)₂].

(b) With hexafluoroisopropylideneamine. An excess of hexafluoroisopropylideneamine (0·42 g., 2·54 mmoles) and tetrakis-(t-butylisocyanide)nickel (0·50 g., 1·2 mmoles) in diethyl ether (25 ml.) were allowed to react at room temperature for 24 hr. The orange yellow solution was filtered and the volume reduced (10 ml.) in vacuo. Addition of hexane (15 ml.) and cooling to -78° afford orange yellow crystals of (II) (0·46 g., 70%), m.p. 128° (dec.) (Found: C, 35·0; H, 3·8; F, 39·0; N, 10·3. C₁₆H₂₀F₁₂N₄Ni requires C, 34·6; H, 3·6; F, 41·0; N, 10·1%), ν_{max} . 3420w (ν_{NH}), 3290w (ν_{NH}), 2207vs (ν_{NC}), 2180vs (ν_{NC}), 1320vw, 1270vw, 1200s, 1180m, 1140s, 1076w, 950w, 940m, 910w, 845w, 803w, 753m, 721m, 712m, and 702m cm.⁻¹. The ¹H n.m.r. spectrum (CDCl₃) showed resonances at τ 6·40br (s, 2H, NH) and

8.86 (s, 18H, Bu^t). The ¹⁹F n.m.r. spectrum (CH₂Cl₂) showed resonances at 66·1 [m, 6F, α -C(CF₃)₂] and 80·6 p.p.m. [m, 6F, β -C(CF₃)₂].

(c) With tetrafluoroethylene. An excess of tetrafluoroethylene (0.25 g., 2.5 mmoles) was condensed (-196°) into a tube containing tetrakis-(t-butylisocyanide)nickel (0.40 g., 1.02 mmoles) dissolved in diethyl ether (25 ml.). After 48 hr. at room temperature, the yellow solution was filtered and the volume was reduced (5 ml.) in vacuo. Addition of hexane (10 ml.) and cooling to -78° gave yellow crystals of (III) (0.32 g., 75%), m.p. 148° (Found: C, 40.0; H, 4.3; F, 35.6; N, 6.5. C₁₄H₁₈F₈N₂Ni requires C, 39.5; H, 4.2; F, 35.8; N, 6.6%), ν_{max} 2230vs (ν_{NC}), 2219vs (ν_{NC}), 1342m, 1261m, 1240m, 1214m, 1154vs, 1098s, 1011s, 970vw, 920vs, 857m, 730m, and 657w cm.⁻¹. The ¹H n.m.r. spectrum (CDCl₃) showed a resonance at τ 8.80 (s, 18H, Bu^t). The ¹⁹F n.m.r. spectrum (Et₂O) showed resonances at 101.6 (s, 4F, α -CF₂) and 138.2 p.p.m. (s, 4F, β -CF₂).

(d) With hexafluorobuta-1,3-diene. Similarly, reaction of hexafluorobuta-1,3-diene (0·24 g., 1·5 mmoles) with tetrakis-(t-butylisocyanide)nickel (0·39 g., 1·0 mmole) in diethyl ether (30 ml.) gave on crystallisation (--78°) from diethyl ether-hexane yellow crystals of (IV) (0·31 g., 80%), m.p. 107° (Found: C, 43·1; H, 4·6; F, 28·0; N, 7·3. C₁₄H₁₈F₆N₂Ni requires C, 43·4; H, 4·6; F, 29·3; N, 7·2%), ν_{max} . 2210vs (ν_{NC}), 2200vs (ν_{NC}), 1750s, 1310vs, 1230m, 1200s, 1150s, 970vs, 930vw, 850w, 829s, and 725m cm.⁻¹. The ¹H n.m.r. spectrum (CDCl₃) showed a resonance at τ 8·50 (s, 18H, Bu^t). The ¹⁹F n.m.r. spectrum (CH₂Cl₂) showed multiplet resonances at 87·5 and 147·7 p.p.m.

(e) With 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene. A solution of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (0.43 g., 2.0 mmoles) in diethyl ether (5 ml.) was added to a stirred (-20°) solution of tetrakis-(t-butylisocyanide)nickel (0.39 g., 1.0 mmole) in diethyl ether (30 ml.). After 3 hr. at -20° the solvent was removed in vacuo and the residue was recrystallised (-78°) from diethyl ether (10 ml.)-hexane (15 ml.) to give crystals of (V) (0.35 g., 80%), m.p. 101° (Found: C, 44.0; H, 4.0; F, 26.0; N, 13.0. C₁₆H₁₈F₆N₄Ni requires C, 43.8; H, 4.1; F, 26.0; N, 12.8%), v_{max.} 2210s (v_{NC}) , 2200vs (v_{NC}) , 2190vs (v_{CN}) , 1400w, 1340m, 1310m, 1272w, 1230vw, 1220w, 1200vs, 1140vs, 1043w, 950s, 920s, 780m, 760w, 770w, 745s, 728vw, and 710s cm.⁻¹. The ¹⁹F n.m.r. spectrum (CH₂Cl₂) showed a singlet at 56.0 p.p.m., while the ¹H n.m.r. signal occurred at τ 8.46 (s, 18H, Bu^t).

(f) With hexafluoropropene. An excess of hexafluoropropene (0.60 g., 4.0 mmoles) was condensed into a tube containing tetrakis-(t-butylisocyanide)nickel (0.39 g., 1.0 mmole) in diethyl ether (25 ml.). After 24 hr. at room temperature the volume of the solvent was reduced (5 ml.) at -20° to give yellow crystals of (VI) (0.22 g., 60%) (unstable), v_{max} 2170s (v_{NC}), 2130vs (v_{NC}), 1295m, 1209m, 1173s, 1120m, 1085m, 1040m, 955s, 765m, 750w, 720w, and 675m cm.⁻¹.

(g) With N-methylhexafluoroisopropylideneamine. Similarly, reaction of tetrakis(t-butylisocyanide)nickel (0.30 g., 0.76 mmole) in diethyl ether (30 ml.) with N-methylhexafluoroisopropylideneamine (0.25 g., 1.4 mmoles) gave on recrystallisation (-78°) from diethyl ether-hexane, orange crystals of (VII) (0.18 g., 65%), v_{max} 3180s, 2160s, 1315vw, 1305vw, 1200m, 1135vw, 1150vw, 1095w, 1050vw, 960m, 940vw, 920vw, 895vw, 870vw, 740vw, 728m, and 680w. Unfortunately the complex was too unstable for analysis but its i.r. spectrum is very similar to that of the platinum analogue.³

^{*} The resonance appears as a singlet due to a quadrupole relaxation.

Reaction of Tetrakis(phenylisocyanide)nickel with Hexafluoroacetone.—An excess of hexafluoroacetone (0.83 g., 5 mmoles) was condensed (-196°) into a tube containing tetrakis(phenylisocyanide)nickel (1.0 g., 2.1 mmoles in diethyl ether (30 ml.). After 70 hr. at room temperature, the yellow solution was filtered and reduced in volume (5 ml.). Addition of hexane (10 ml.), and cooling to -78°, gave yellow crystals of (VIII) (0.56 g., 65%), m.p. 73° (Found: C, 47.1; H, 2.6; N, 6.7. C₁₇H₁₀F₆N₂NiO requires C, 47.3; H, 2.3; N, 6.5%), v_{max} 2179s (v_{NC}), 2150 (v_{NC}), 1585w, 1338m, 1315s, 1220w, 1200vw, 1170w, 1150vw, 1119w, 1070vw, 1020vw, 1000vw, 946s, 924w, 840m, 758s, 750m, 728w, 715s, 690m, and 646vw cm.⁻¹. The ¹H n.m.r. spectrum (CDCl₃) showed a resonance at τ 2.45 (m, 10H, C₆H₅). The ¹⁹F n.m.r. spectrum (Et₂O) showed a resonance at 67.7 p.p.m. (s, 6F, CF₃).

Reaction of Phenyl Isocyanide with Hexafluoroacetone-(cyclo-octa-1,5-diene)nickel.—Phenyl isocyanide (0.41 g., 4 mmoles) was added to a stirred solution of hexafluoroacetone(cyclo-octa-1,5-diene)nickel ⁸ (0.67 g., 2 mmoles) in diethyl ether (20 ml.) at 0°. After 1 hr. at 0° the yellow solution was filtered, reduced in volume (5 ml.), and hexane added to give at -78° yellow crystals of (VIII) (0.66 g., 75%), identical (m.p., i.r., ¹⁹F n.m.r. spectrum) to that described above.

Reaction of t-Butyl Isocyanide with Hexafluoroacetone-(cyclo-octa-1,5-diene)nickel. A solution of t-butyl isocyanide (0·12 g., 1·5 mmole) in diethyl ether (5 ml.) was added to hexafluoroacetone(cyclo-octa-1,5-diene)nickel (0·20 g., 0·6 mmole) in ether (20 ml.) at -20° . After 2 hr. the yellow solution was filtered, reduced in volume (5 ml.), and hexane (10 ml.) was added to it; on cooling to -78° it afforded yellow crystals of (IX) (0·21 g., 90%), m.p. 130° (Found: C, 40·3; H, 4·6; N, 7·4. C₁₃H₁₈F₆N₂NiO requires C, 40·0; H, 4·6; N, 7·2%), ν_{max} 2199s (ν_{NC}), 2183vs (ν_{NC}), 1315s, 1268vw, 1238vw, 1190vs, 1135s, 1098m, 943vw, 845s, 753m, 730vw, 710s, and 640vs cm⁻¹. The ¹H n.m.r. spectrum [(CD₃)₂CO] showed a resonance at τ 8·56 (s, 18H, Bu^t). The ¹⁹F n.m.r. spectrum (Et₂O) showed a resonance at 66·6 p.p.m. (s, 6F, CF₃).

Reaction of t-Butyl Isocyanide with Hexafluoroisopropylideneamine(cyclo-octa-1,5-diene)nickel.— Hexafluoroisopropylideneamine (0.60 g., 3.6 mmoles) was condensed (-196°) into a tube containing a suspension of bis(cycloocta-1,5-diene)nickel (0.70 g., 2.54 mmoles) in diethyl ether (30 ml.). After 90 hr. at 0° the red solution was filtered and the solvent was removed in vacuo at -20° . The residue was dissolved in diethyl ether (25 ml.) and hexane (10 ml.). t-Butyl isocyanide (0.42 g., 5.1 mmoles) was added at -10° and the reaction mixture was stirred for 2 hr. at -10° . The solvent was removed in vacuo and the residue was recrystallised (-78°) from diethyl ether (10 ml.) hexane (20 ml.) to give yellow crystals of (X) (0.61 g., 70%), m.p. 80° (dec.) (Found: C, 40.4; H, 4.4; N, 10.5. $C_{13}H_{19}F_6N_3Ni$ requires C, 40.0; H, 4.9; N, 10.8%), ν_{max} . 3190m ($v_{\rm NH}$), 2182s ($v_{\rm NC}$), 2150s ($v_{\rm NC}$), 1325m, 1190s, 1120s, 930m, 919m, 810m, 770w, 750m, 730w, 700m, and 645vw cm.⁻¹. The ¹H n.m.r. spectrum [(CD₃)₂CO] showed resonances at τ 6.90 (s, 1H, NH) and 8.58 (s, 18H, Bu^t). The ¹⁹F n.m.r. spectrum (Et₂O) showed a resonance at 64·1 p.p.m. (s, 6F, CF₃).

Reactions of Hexafluoroacetonebis-(t-butylisocyanide)nickel (IX).—(a) With hexafluoroacetone. An excess of hexafluoroacetone (0.166 g., 1.0 mmole) was condensed (-196°) into a tube containing hexafluoroacetonebis-(t-butyliso-

cyanide)nickel (0.19 g., 0.5 mmole) in diethyl ether (30 ml.). After 4 days at room temperature the yellow solution was filtered and the volume was reduced (5 ml.) *in vacuo*. Hexane (15 ml.) was added to give on cooling to -78° yellow crystals of (I) (0.13 g., 60%) identical (m.p., i.r., ¹⁹F n.m.r. spectrum) to that described above.

(b) With hexafluoroisopropylideneamine. Similarly, reaction of hexafluoroisopropylideneamine (0.25 g., 1.5 mmole) with hexafluoroacetonebis-(t-butylisocyanide)nickel (0.39 g., 1 mmole) in diethyl ether (40 ml.) gave on recrystallisation (-78°) from hexane-diethyl ether yellow crystals of (XIb) (0.45 g., 80%), m.p. 158° (Found: C, 34.7; H, 3.4; N, 7.6. C₁₆H₁₉F₁₂N₃NiO requires C, 34.5; H, 3.4; N, 7.5%), ν_{max} . 3421m (ν_{NH}), 2230vs (ν_{NC}), 2220vs (ν_{NC}), 1250s, 1190s, 1140s, 1070w, 950s, 930m, 918m, 830m, 802m, 750w, 720s, and 700s cm.⁻¹. The ¹H n.m.r. spectrum (CDCl₃) showed resonances at 7.65 (s, 1H, NH) and 8.58 (s, 18H, Bu^t). The ¹⁹F n.m.r. spectrum (CH₂Cl₂) showed resonances at 65.4 [m, 6F, α -C(CF₃)₂] and 80.7 p.p.m. [m, 6F, β -C(CF₃)₂].

(c) With tetrafluoroethylene. In a similar way, tetrafluoroethylene (0.2 g., 2 mmoles) was treated with hexafluoroacetonebis-(t-butylisocyanide)nickel (0.19 g., 0.5mmole) in ether (20 ml.). After 10 days at 55°, the yellow solution was filtered and the volume was reduced (5 ml.) in vacuo. On cooling (-78°), after addition of hexane, yellow crystals were obtained consisting of a mixture of (IX) and (III).

Reactions of Hexafluoroisopropylideneaminebis-(t-butylisocyanide)nickel (X).—(a) With hexafluoroisopropylideneamine. Reaction of hexafluoroisopropylideneamine (0.3 g., 1.8mmoles) with hexafluoroisopropylideneaminebis-(t-butylisocyanide)nickel (0.20 g., 0.51 mmole) in diethyl ether (25ml.) for 2 days at room temperature gave after recrystallisation (-78°) from diethyl ether-hexane yellow crystals of (II) (0.23 g., 80%), identical (m.p., i.r., ¹⁹F n.m.r. spectrum) to that described above.

(b) With hexafluoroacetone. Reaction of hexafluoroacetone (0.3 g., 1.8 mmoles) with hexafluoroisopropylideneaminebis(t-butylisocyanide)nickel (0.20 g., 0.51 mmole) in diethyl ether (20 ml.) and hexane (5 ml.) gave after 24 hr. at room temperature yellow crystals of (XIb) (0.15 g., 55%), identical (m.p., i.r., ¹⁹F n.m.r. spectrum) to that described above. The solvent from the filtrate was reduced in volume (5 ml.). Addition of hexane (10 ml.) and cooling (-78°) afforded yellow crystals of (XIa) (0.04 g., 15%), m.p. 146° (Found: C, 34.2; H, 3.6; N, 8.1. C₁₆H₁₉F₁₂N₃NiO requires C, 34.5; H, 3.4; N, 7.5%), v_{max} , 3421m (v_{NH}), 2230vs $(v_{\rm NC})$, 2220vs $(v_{\rm NC})$, 1250s, 1190s, 1140s, 1070w, 950s, 930m, 918m, 830m, 802m, 750w, 720s, and 700s cm.⁻¹. The ¹H n.m.r. spectrum (CDCl₃) showed resonances at τ 7.65 (s, 1H, NH) and 8.58 (s, 18H, Bu^t). The ¹⁹F n.m.r. spectrum (CH_2Cl_2) showed resonances at 64.60 [m, 6F, α -C(CF₃)₂] and 81·1 p.p.m. [m, 6F, β-C(CF₃)₂].

(c) With tetrafluoroethylene. Reaction of tetrafluoroethylene (0.3 g., 3 mmoles) with hexafluoroisopropylideneaminebis-(t-butylisocyanide)nickel (0.20 g., 0.51 mmole) in diethyl ether (20 ml.) for 2 days at room temperature gave after reduction in volume (5 ml.), addition of hexane (10 ml.), and cooling (-78°), yellow crystals of (III) (0.15 g., 70_{\circ}), identical (m.p., i.r., ¹⁹F n.m.r. spectrum) to that described above.

Reaction of Hexafluoroacetonebis(phenylisocyanide)nickel (VIII) with Hexafluoroisopropylideneamine.—An excess of

hexafluoroisopropylideneamine (0·3 g., 1·8 mmoles) was treated with hexafluoroacetonebis(phenylisocyanide)nickel (0·35 g., 0·8 mmole) in diethyl ether (20 ml.). After 2 days at room temperature, the yellow solution was filtered and reduced in volume (5 ml.). Addition of hexane (10 ml.) and cooling (-78°) gave yellow crystals of (XII) (0·30 g., 70%), m.p. 93° (Found: C, 40·5; H, 1·9; N, 7·3. C₁₈H₁₁F₁₂N₃NiO requires C, 40·3; H, 1·8; N, 7·1%), ν_{max} . 3410m (ν_{NH}), 2224vs (ν_{NC}), 2200vs (ν_{NC}), 1590w, 1260m, 1230m, 1210s, 1190s, 1170m, 1150s, 1135m, 1080w, 1030vw, 1005w, 960m, 930m, 807w, 762s, 723m, 708m, and 690m cm.⁻¹. The ¹H n.m.r. spectrum (CDCl₃) showed resonances at $\tau 2.65$ (m, 10H, C₆H₅) and 7·60 (s, 1H, NH). The ¹⁹F n.m.r. spectrum (Et₂O) showed resonances at 66·8 [m, 6F, α -C(CF₃)₂] and 82·1 p.p.m. [m, 6F, β -C(CF₃)₂].

Reactions of Peroxobis-(t-butylisocyanide)nickel.-(a) With one mole of hexafluoroacetone. Hexafluoroacetone (0.14 g., 0.8 mmole) was introduced into a flask fitted with a solid CO₂ condenser, containing peroxobis-(t-butylisocyanide)nickel (0.21 g., 0.8 mmole) in diethyl ether (20 ml.) and hexane (10 ml.) at -50° . After 2 hr. at -50° , the solvent was removed in vacuo, and the pale yellow solid was washed with hexane (10 ml.) at -30° before being dried in vacuo at -30° to give crystals of (XIII) (0.30 g., 90%), m.p. 75-78° (dec. explosively) (Found: C, 31.9; H, 4.2; F, 26.6; N, 6.6. C₁₃H₁₈F₆N₂NiO₃ requires C, 36.8; H, 4.3; F, 26.9; N, 6.6%), ν_{max} 2980m, 2940w, 2880vw, 2240vs ($\nu_{NC}),$ 2228vs (v_{NC}), 1460m, 1405w, 1380m, 1315m, 1300m, 1240w, 1200vs, 1168s, 1155w, 1080vw, 1060s, 973s, 900m, 855w, 750w, 722m, 650w, 630w, and 622w cm.⁻¹. The ¹H n.m.r. spectrum (CDCl₃ at -30°) showed a resonance at $\tau 8.60$ (s, 18H, Bu^t). The ¹⁹F n.m.r. spectrum (Et₂O at -40°)

showed a resonance at 82.6 p.p.m. (s, 6F, CF₃), and in CH₂Cl₂ at -40° a resonance at 82.7 p.p.m.

(b) With four moles of hexafluoroacetone. A similar reaction with hexafluoroacetone (0.39 g., 2.4 mmoles) and peroxobis-(t-butylisocyanide)nickel (0.15 g., 0.6 mmole) in ether (20 ml.)-hexane (8 ml.) at -50° gave, after recrystallisation (-78°) from ether, yellow crystals of (XIV) (0.24 g., 70%), m.p. 85-90° (dec.) (Found: C, 31.4; H, 3.6; N, 4.7. C₁₆H₁₈F₁₂N₂NiO₄ requires C, 32.5; H, 3.1; N, 4.7%), v_{max.} 2220vs (v_{NC}), 2200s (v_{NC}), 1670s, 1298s, 1200vs, 1150w, 1080s, 1050w, 1020m, 960vs, 900w, 855m, 800m, 730vs, 710m, and 670vw cm.⁻¹. The ¹H n.m.r. spectrum (CDCl₃ at -30°) showed a resonance at τ 8.68 (s, 18H, Bu^t). The ¹⁹F n.m.r. spectrum (Et₂O at -30°) showed resonances at 82.5 (s, 6F, CF₃) and 83.5 p.p.m. (s, 6F, CF₃).

Reaction of Compound (XIII) with Diethyl Ether.—A suspension of (XIII) (0.10 g., 0.23 mmole) in diethyl ether (8 ml.) was stirred at 0° for $1\frac{1}{2}$ hr. The solvent was removed in vacuo at -30° to give yellow crystals of (XV) (0.078 g., 85%), m.p. 105° (dec.) (Found: C, 38.4; H, 4.8; N, 7.3. C₁₃H₁₈F₆N₂NiO₂ requires C, 38.3; H, 4.4; N, 6.9%), v_{max} . 2240vs (v_{NC}), 2227vs (v_{NC}), 1300m, 1240m, 1218s, 1200vs, 1168m, 1150w, 1080vw, 1060m, 974s, 960s, 855w, 750m, 743m, and 722s cm.⁻¹. The ¹H n.m.r. spectrum (CDCl₃ at -40°) showed a resonance at $\tau 8.60$ (s, 18H, Bu^t). The ¹⁹F n.m.r. spectrum (CHCl₃ at -40°) showed a resonance at 79.91 p.p.m. (s, 6F, CF₃), and at room temperature a resonance at 79.30 p.p.m.

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