Reactions of Low-Valent Metal Complexes with Fluorocarbons. Part XXIX.[1] Zerovalent Nickel and Platinum Complexes with Hexafluorobut-2-yne and Hexakis(trifluoromethyl)benzene

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Reaction of [Pt(*trans*-stilbene)$(PEt_3)_2$] with $C_6(CF_3)_6$ affords a complex [Pt{$C_6(CF_3)_6$}$(PEt_3)_2$], shown by variable temperature ^{19}F n.m.r. spectroscopy to be a fluxional molecule. Treatment of the related nickel complexes [Ni{$C_6(CF_3)_6$}L_2] (L = $AsMe_2Ph$ or $P(OMe)_3$) with an excess of $CF_3C{\equiv}CCF_3$ yields a new kind of complex: a hexakis(trifluoromethyl)nickelacyclohepta-*cis,trans,cis*-triene. Reaction of [Pt{$C_2(CF_3)_2$}$(PEt_3)_2$] with excess of hexafluorobut-2-yne proceeds more slowly to afford a monophosphine substituted hexakis(trifluoromethyl)-platinacyclohepta-*cis,trans,cis*-triene, which with $Ph_2PCH_2CH_2PPh_2$ gives a complex isostructural with the nickel systems.

THERE has been considerable interest in the reactions of acetylenes with low-valent transition metal complexes, and in particular, in the formation of substituted benzenes from acetylenes in what in some cases have been shown to be catalytic reactions. We have previously reported[2] that the reaction of hexafluorobut-2-yne with bis(cyclo-octa-1,5-diene)nickel affords a mononuclear complex [Ni{$C_6(CF_3)_6$}(1,5-C_8H_{12})] and a dinuclear species [Ni_2{$C_6(CF_3)_6$}(1,5-$C_8H_{12})_2$]. The reaction of the mononuclear complex with, for example, triphenylphosphine, trimethyl phosphite, or dimethylphenylarsine (L) resulted in displacement of cyclo-octa-1,5-diene and formation of the stable complexes [Ni{$C_6(CF_3)_6$}L_2]. These complexes are the only nickel–arene compounds to have been described so far, and the appearance in their ^{19}F n.m.r. spectra of a single temperature invariant resonance raised the important problem as to the nature of the bonding between the nickel atom and the C_6 ring. Attempts to obtain suitable crystals of one or other of the nickel compounds for *X*-ray crystallography studies were unsuccessful, and therefore attention was turned to the possibility of preparing an analogous platinum complex, with the additional interest that if a degenerate dynamic process was occurring with these species, then this process might have a higher activation energy in the case of the platinum system.

The relative inaccessibility of [Pt(1,5-$C_8H_{12})_2$] precluded investigation of its reactions with hexafluorobut-2-yne, however, as previously observed,[2] complex

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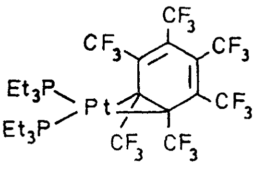
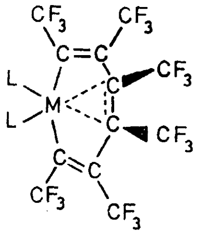
[1] Part XXVIII, J. Clemens, M. Green, and F. G. A. Stone, preceding paper.

[2] J. Browning, C. S. Cundy, M. Green, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1971, 448.

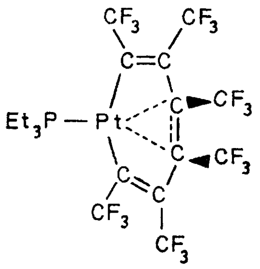
[Ni{C$_6$(CF$_3$)$_6$}(PPh$_3$)$_2$] can also be obtained directly by treating [Ni(C$_2$H$_4$)(PPh$_3$)$_2$] with hexakis(trifluoromethyl)benzene; a process which may be formally considered as an oxidative-elimination reaction. The high nucleophilicity of tris(triethylphosphine)platinum has been commented on by Muetterties and co-workers,[3] and as part of a separate investigation we had prepared this zerovalent platinum complex by a more convenient route, and as detailed in the experimental section found that *trans*-stilbenebis(triethylphosphine)platinum can be readily prepared from [Pt(PEt$_3$)$_3$].



(I)



(IV) M=Ni, L=AsMe$_2$Ph
(V) M=Ni, L=P(OMe)$_3$
(VIII) M=Pt, L$_2$=diphos



(VII)

Reaction of *trans*-stilbenebis(triethylphosphine)platinum with hexakis(trifluoromethyl)benzene in toluene at 55 °C afforded a moderate yield of a complex (I), characterised by elemental analysis, i.r. and n.m.r. spectroscopy as hexakis(trifluoromethyl)benzenebis(triethylphosphine)platinum. The ^{19}F n.m.r. spectrum (30°) showed a single apparent triplet resonance with ^{195}Pt satellite triplets centred at 51·2 p.p.m. (rel. CCl$_3$F, 0·0 p.p.m.). On cooling, the triplet resonance collapsed, and at −90° was replaced by two unresolved multiplets centred at 47·7 and 52·5 p.p.m., with relative intensity 1 : 2 respectively. These observations do not establish the structure of (I), so that in order to learn more about the nature of this complex a single crystal *X*-ray diffraction study was carried out elsewhere.[4] The solid state structure is as illustrated, with the Pt(PEt$_3$)$_2$ group bonded to two adjacent carbon atoms of a non-planar C$_6$ ring; the dihedral angle between the mean plane of this ring and the group $\overline{\mathrm{Pt{\cdot}C(CF_3)C}}$(CF$_3$) being 102°. The C–C bond distances of the C$_6$ ring alternate between average values consistent with single and double bonds, with the exception of the C–C bond length of the carbons bonded to the platinum, which was significantly lengthened as a result of co-ordination. This bond lengthening has been previously observed to occur on co-ordination of a wide variety of unsaturated systems.[5]

If the assumption is made that the instantaneous structure of (I) in solution is the same as that established in the solid state then it is clear that the complex [Pt{C$_6$(CF$_3$)$_6$}(PEt$_3$)$_2$] undergoes in solution a low activation energy degenerate molecular rearrangement process of a kind not previously observed, and it seems likely that a similar but faster fluxional process occurs with the analogous nickel system.

The 1—2η bonding mode found for the platinum complex (I) contrasts with the 1—4-η bonding established in the solid state by *X*-ray crystallography for hexakis(trifluoromethyl)benzene(π-cyclopentadienyl)rhodium,[6] a complex which does not show fluxional behaviour. Recently, it has been reported[7] that the related complex [Rh(η-C$_5$Me$_5$){C$_6$(CO$_2$Me)$_6$}] shows fluxional behaviour only at a high temperature (155 °C). It is interesting that in these rhodium systems, and with the related ruthenium complex [Ru{C$_6$(CF$_3$)$_6$}(CO)$_2${P(OMe)$_3$}] which also does not show fluxional behaviour,[8] the metal may be considered to be co-ordinatively saturated unlike the platinum and nickel complexes which may be considered as 16-electron co-ordinatively unsaturated species.

The ^{19}F n.m.r. spectrum of (I) studied at −90° clearly does not represent the instantaneous structure and therefore a variable temperature line shape analysis and detailed mechanistic discussion is not possible. However, it is worthwhile briefly to consider possible mechanisms for the fluxional process. The appearance of ^{19}F^{195}Pt coupling in the room temperature ^{19}F n.m.r. spectrum of (I) excludes the possibility of a dissociative process.

As was previously[2] discussed in the case of the analogous nickel system a mechanism (A, Scheme 1) involving the formation of a symmetrically bonded species in which the platinum is equally bonded to all six carbon atoms of the C$_6$ ring, seems most unlikely as this would require a violation of the 18-electron rule.

Moreover, a reaction path of the kind considered[2] for the nickel system, in which the nickel or platinum is bonded in the 1,4 mode now seems most unlikely in view of the structural studies with (I). This leaves two extreme mechanisms (B and C) for the degenerate intramolecular rearrangement of (I). Mechanism (B) in-

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[3] D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1971, **93**, 3543.

[4] J. Browning, M. Green, B. R. Penfold, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1973, 31.

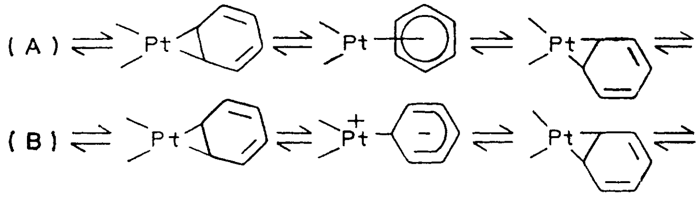
[5] J. H. Nelson and H. B. Jonassen, *Co-ordination Chem. Rev.*, 1971, **6**, 27.

[6] M. R. Churchill and R. Mason, *Proc. Roy. Soc.*, 1966, *A*, **292**, 61.

[7] J. W. Kang, R. F. Childs, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1970, **92**, 720.

[8] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2981.

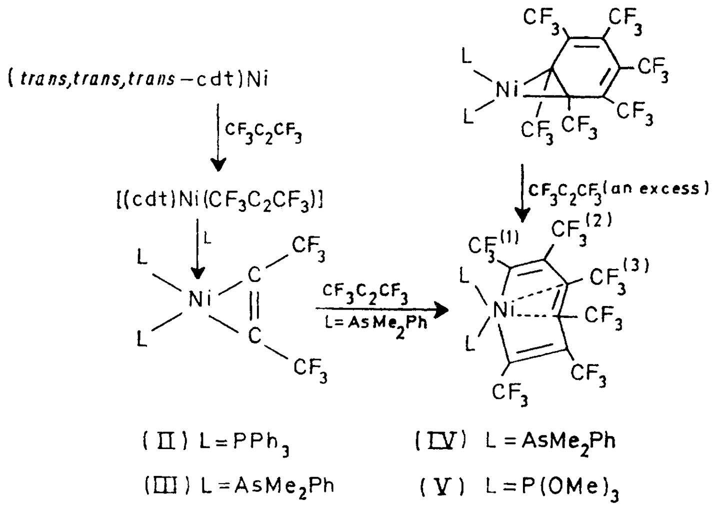
volves the formation of a dipolar intermediate (Scheme 1). Whereas for (C) one could think in terms of a concerted process in which overlap between the empty platinum d_{z^2} orbital and the filled π-orbitals of the C_6 ring plays an important part. However, it is not possible on the basis of the presently available evidence to distinguish between these alternative reaction paths.



Scheme 1 CF_3 Groups omitted for clarity

The formation of benzene derivatives from metallocyclopentadienes, which in turn are formed from so-called metallocyclopropene complexes, is well established,[9-11] and in attempting to obtain evidence for such intermediates in the formation of the nickel complex $[Ni\{C_6(CF_3)_6\}L_2]$ an unusual reaction was discovered.

The complex $[Ni(CF_3C_2CF_3)(PPh_3)_2]$ (II) does not react with more hexafluorobut-2-yne, however, the corresponding dimethylphenylarsine analogue, (III), prepared by treating *trans,trans,trans*-cyclododeca-1,5,9-trienenickel with the but-2-yne at low temperatures followed by addition of $AsPhMe_2$ in the absence of the acetylene, reacts with $CF_3C{\equiv}CCF_3$ in toluene at room temperature to afford an orange crystalline complex (IV). The latter can also be prepared by treating the isomeric compound hexakis(trifluoromethyl)benzene(dimethylphenylarsine)nickel with at least three molar equivalents of hexafluorobut-2-yne (Scheme 2). It was found that an analogous reaction occurred on treatment of hexakis(trifluoromethyl)benzenebis(trimethyl phosphite)nickel with $CF_3C{\equiv}CCF_3$ to form yellow crystals of (V).



Scheme 2

Elemental analyses and solution molecular weight measurements established the molecular formula of the complexes (IV) and (V). However, the appearance of double bond absorption bands in the i.r. spectra at respectively **1639**m and **1652**m cm^{-1}, together with the presence in the ^{19}F n.m.r. spectra of three resonances, which in conjunction with decoupling experiments (see Experimental section) indicated the presence of the arrangement $NiC(CF_3)C(CF_3)C(CF_3)$, showed that these complexes had an unusual structure. An X-ray diffraction study[4] of (V) established the illustrated structure, and allowed a detailed interpretation of the n.m.r. spectra. Thus (IV) and (V) may be described as nickelahexakis(trifluoromethyl)cyclohepta-*cis,trans,-cis*-triene complexes. Interatomic distances suggest there is a significant interaction between the nickel and the central *trans*-double bond.

In view of these findings the analogous platinum chemistry was investigated. Reaction of hexafluorobut-2-yne with *trans*-stilbenebis(triethylphosphine)platinum afforded the complex hexafluorobut-2-ynebis(triethylphosphine)platinum (VI), which showed the expected strong i.r. band at **1745** cm^{-1} and characteristic n.m.r. parameters.[10,11]

Heating (**90** °C) complex (VI) with an excess of hexafluorobut-2-yne afforded after a difficult separation procedure a small amount (*ca.* 10% yield) of a yellow complex (VII). This same complex was also obtained on heating compound (I) with hexafluorobut-2-yne.

Although, the ^{19}F n.m.r. spectrum of (VII) showed the three resonances expected for a platinum analogue of the nickel complexes (IV) and (V), a detailed examination of the ^{19}F spectrum and elemental analysis showed that (VII) had the illustrated structure in which only one co-ordinated triethylphosphine is present. Further support for this was obtained by reacting (VII) with $(Ph_2PCH_2)_2$, which resulted in the displacement of triethylphosphine and the formation of (VIII). Decoupling experiments (see Experimental section) and detailed comparison of the chemical shift data of (VIII) with that of (IV) and (V) showed that these complexes are isostructural.

The formation of these metallocycloheptatrienes is particularly interesting and cannot be readily accommodated by reaction paths not involving ionic or radical intermediates. It is hoped that further experiments will elucidate how (IV), (V), (VII), and (VIII) are formed.

Finally it may be mentioned that the establishment of the structure of (I) by X-ray crystallography strongly suggests that the binuclear complexes $[Ni_2\{C_6(CF_3)_6\}L_4]^2$ have a molecular structure related to that of (I) with the nickel atoms on opposite sides of the $C_6(CF_3)_6$ ring.

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[9] J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, 1968, **7**, 1298.

[10] Beverley Clarke, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 951.

[11] S. K. Shakshooki, Ph.D. Thesis, Bristol University, 1971.

EXPERIMENTAL

^{1}H and ^{19}F N.m.r. spectra were recorded on a Varian HA 100 spectrometer at 100 and 94·1 MHz respectively. Heteronuclear INDOR measurements on ^{31}P and ^{195}Pt nuclei were carried out as previously described,[12] with ^{195}Pt shifts being expressed relative to a standard frequency of 21·4 MHz, corrected to Me_4Si resonating at 100 MHz. All *J*(PPt) values reported are from the more precise ^{1}H{^{31}P} or ^{19}F{^{31}P} INDOR measurements. I.r. spectra were recorded with Perkin-Elmer 257 and 457 spectrophotometers. Reactions, except those in sealed tubes, were conducted in a dry nitrogen atmosphere.

Preparation of trans-*Stilbenebis(triethylphosphine)platinum.*—A solution of *trans*-stilbene (0·75 g, 4·2 mmol) in toluene (10 ml) was added to tris(triethylphosphine)platinum (2·14 g, 3·89 mmol) contained in a Schlenk tube. Volatile material was slowly removed *in vacuo*, and the orange residue warmed to 65 °C for 50 min. The residue was redissolved in toluene and the evaporation sequence repeated. The resultant yellow solid was dissolved in light petroleum–toluene (5 : 3) filtered through Florisil, and cooled (−10°), giving pale yellow crystals of trans-*stilbenebis(triethylphosphine)platinum* (1·40 g, 59%), m.p. 113—115° (Found: C, 51·7; H, 6·9. $C_{26}H_{42}P_2Pt$ requires C, 51·1; H, 6·9), $\nu_{max.}$ (Nujol) 3075w, 3055w, 3030sh, 3016w, 1598s, 1575w, 1491s, 1414m, 1328vw, 1300vw, 1245m, 1212m, 1172w, 1152w, 1138w, 1069m, 1028s, 995m, 889w, 761sh, 752s, 749sh, 731m, 716m, and 692vs cm^{-1}; ^{1}H n.m.r. resonances (C_6D_6) at τ 2·8 (m, 10H, C_6H_5), 6·12 [m, 2H, CH=CH, *J*(HP) 2·0 Hz, *J*(PtH) 54·0 Hz], 8·62 [m, 12H, $\mathit{PCH_2}CH_3$] and 9·2 [m, 18H, $PCH_2\mathit{CH_3}$]; ^{1}H{^{195}Pt} INDOR δ_{Pt} +589 p.p.m. [*J*(PPt) 3548 Hz].

Preparation of Complex (III), *Hexafluorobut-2-ynebis(dimethylphenylarsine)nickel.*—An excess of hexafluorobut-2-yne (8 mmol) was condensed (−196°) into a Schlenk tube (100 ml) containing cyclododeca-*trans,trans,trans*-trienenickel (1·0 g, 4·5 mmol) partially dissolved in diethyl ether (10 ml). The tube and contents were allowed to warm to −78° and left at this temperature for 4 h. Excess of hexafluorobut-2-yne was removed *in vacuo*, and dimethylphenylarsine (1·66 g, 9·0 mmol) added in toluene (6 ml). Yellow crystals were deposited on warming to room temperature and reduction of the volume of the solvent *in vacuo*. The crystals were washed with diethyl ether at −78° to give the air- and heat-sensitive complex (III) (1·0 g, 38%) (Found: C, 41·2; H, 3·9. $C_{20}H_{22}F_6As_2Ni$ requires C, 41·1; H, 3·8%), $\nu_{max.}$ (Nujol) 3070w, 3055w, 3030w, 1788m, 1585w, 1484m, 1438s, 1160m, 1145sh, 1142sh, 1136sh, 1125s, 1118s, 1085m, 1070sh, 1025w, 1000w, 975w, 970w, 923m, 912sh, 905m, 865sh, 858m, 845sh, 810m, 740s, 700s, 693m, 675w, and 650m cm^{-1}. The ^{19}F n.m.r. spectrum (toluene) showed a single resonance at 53·2 p.p.m. (m, 6F).

Preparation of Complex (II), *Hexafluorobut-2-ynebis(triphenylphosphine)nickel.*—A similar reaction of hexafluorobut-2-yne (8 mmol) with *trans,trans,trans*-cyclododeca-1,5,9-trienenickel (1·0 g, 4·5 mmol) gave on addition of triphenylphosphine the complex (II), identical (i.r., n.m.r.) with that described in the literature.[13]

Preparation of Complex (VI), *Hexafluorobut-2-ynebis(triethylphosphine)platinum.*—An excess of hexafluorobut-2-yne (5 mmol) was condensed into a Schlenk tube (150 ml) containing a solution of *trans*-stilbenebis(triethylphosphine)platinum (1·83 g, 3·0 mmol) in toluene (25 ml). The mixture was warmed to −10°, and allowed to stand for 1 h before warming to room temperature and removal of solvent *in vacuo*. The solid residue was transferred to a sublimation apparatus and *trans*-stilbene removed (60°, 0·02 mmHg). The residue was chromatographed on a Florisil packed column. Elution with light petroleum gave crystals of complex (VI) (1·20 g, 67%) m.p. 82—83° (Found: C, 32·4; H, 5·1. $C_{16}H_{30}F_6P_2Pt$ requires C, 32·4; H, 5·1%), $\nu_{max.}$ (Nujol) 1745s, 1285w, 1262s, 1218vs, 1110vs, 1050m, 1040sh, 1034m, 920w, 815m, 762m, 752m, and 685m cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 8·15 (m, 12H, $\mathit{PCH_2}CH_3$) and 8·96 (m, 18H, $PCH_2\mathit{CH_3}$); ^{19}F n.m.r. resonance ($CDCl_3$) at 54·95 p.p.m. [complex system with ^{195}Pt satellites, |*J*(PF *trans*) + *J*(PF *cis*)| 11 Hz, *J*(PtF) 65 Hz]; ^{19}F{^{195}Pt} INDOR δ_{Pt} + 179 p.p.m. [*J*(PPt) 3413 Hz].

Preparation of (I), *Hexakis(trifluoromethyl)benzenebis(triethylphosphine)platinum.*—A solution of *trans*-stilbenebis(triethylphosphine)platinum (1·0 g, 1·6 mmol) and hexakis(trifluoromethyl)benzene (0·98 g, 2 mmol) in toluene (35 ml) was stirred for 4 h at 55 °C, and a further 16 h at room temperature. Removal of solvent *in vacuo* gave an orange solid from which *trans*-stilbene and the excess of hexakis(trifluoromethyl)benzene were sublimed (65 °C, 0·01 mmHg). The residue was chromatographed on a Florisil packed column. Elution with diethyl ether–light petroleum (4 : 1) gave orange crystals of (I) (0·65 g, 44%) m.p. 203° (Found: C, 31·1; H, 2·9; P, 6·5; F, 39·3. $C_{24}H_{30}F_{18}P_2Pt$ requires C, 31·4; H, 3·3; P, 6·7; F, 37·3%), $\nu_{max.}$ (Nujol) 1569w, 1501m, 1421m, 1379m, 1348m, 1305sh, 1289m, 1255sh, 1248s, 1220vs, 1200vs, 1173vs, 1155sh, 1125m, 1117m, 1041m, 1020w, 809vw, 765m, 738w, 722m, 709w, 691vw, and 645m cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 8·11 (m, 12H, $P\mathit{CH_2}CH_3$) and 8·99 (m, 18H, $PCH_2\mathit{CH_3}$); ^{19}F n.m.r. resonance (CH_2Cl_2) at 51·2 p.p.m. [t with ^{195}Pt satellites, 18F, *J*(PF) 3Hz, *J*(PtF) 27 Hz]; ^{19}F{^{195}Pt} INDOR ($CDCl_3$), δ_{Pt} + 105 p.p.m. [*J*(PPt) 3805 Hz].

Reaction of Complex (III) *with Hexafluorobut-2-yne.*—An excess of hexafluorobut-2-yne (4 mmol) was condensed into a Carius tube containing a solution of (III) (0·2 g, 0·34 mmol) in toluene (15 ml). After 6 h at room temperature the brown-yellow solution became a clear bright red. The volume of the solvent was reduced *in vacuo* and the solution cooled (−78°) to give white crystals of hexakis(trifluoromethyl)benzene (0·2 g, 0·41 mmol). The supernatant liquid was removed and the volume further reduced. The resultant crystals were recrystallised from diethyl ether–light petroleum to yield air-stable orange *crystals* of (IV) (0·3 g, 96%) m.p. 162—163° [Found: C, 37·3; H, 2·3; As, 17·0; *M*, 678 (acetone). $C_{28}H_{22}F_{18}As_2Ni$ requires C, 37·5; H, 2·4; As, 16·6%; *M*, 909], $\nu_{max.}$ (Nujol) 3080w, 3060w, 2970w, 2955w, 2930w, 2860w, 1648sh, 1639m, 1581w, 1485w, 1465w, 1455w, 1437w, 1414w, 1331s, 1308m, 1278w, 1272w, 1250s, 1231s, 1195s, 1180s, 1162s, 1154s, 1141s, 1133sh, 1124s, 1118s, 1102m, 1084w, 1074w, 1051w, 1028w, 1002w, 950w, 940w, 909w, 877m, 873m, 801w, 764w, 748m, 742m, 721w, 699m, 685w, and 663w cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 2·74 (s, 5H, C_6H_5As) and 8·59 (d, 6H, CH_3As); ^{19}F n.m.r. re-

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[12] P. L. Goggin, R. J. Goodfellow, J. R. Knight, M. G. Norton, and B. F. Taylor, *J.C.S. Dalton*, 1973, 2220.

[13] E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Canad. J. Chem.*, 1968, **46**, 3879.

sonances (CH_2Cl_2) at 53·82 p.p.m. [q, 6F, $CF_3^{(1)}$, *J*(FF) 8 Hz], 54·8 [q, 6F, $CF_3^{(3)}$, *J*(FF) 6 Hz] and 64·7 [m, 6F, $CF_3^{(2)}$]. Double irradiation of the signal at 64·7 p.p.m. collapsed the other signals to singlets, and irradiation of the signal at 54·8 p.p.m. collapsed the signal at 64·7 p.p.m. to a quartet [*J*(FF) 8·0 Hz].

An identical material was obtained from hexakis(trifluoromethyl)benzenebis(dimethylphenylarsine)nickel (0·3 g, 0·33 mmol) in toluene (15 ml) by reaction (12 h) with hexafluorobut-2-yne (3 mmol) at room temperature. Removal of the solvent *in vacuo* gave hexakis(trifluoromethyl)benzene (0·20 g, 0·4 mmol) and complex (IV) (0·28 g, 93%).

Reaction of Hexafluorobut-2-yne with Hexakis(trifluoromethyl)benzenebis(trimethyl phosphite)nickel.—Hexafluorobut-2-yne (3 mmol) was condensed (−196°) into a Carius tube (50 ml) containing hexakis(trifluoromethyl)benzenebis(trimethyl phosphite)nickel (0·3 g, 0·38 mmol) partially dissolved in toluene (15 ml). After one week at room temperature, the solution was filtered to remove a small amount of nickel, the solvent reduced *in vacuo*, and cooled (−10°). The precipitated hexakis(trifluoromethyl)benzene was filtered off, and solvent removed from the supernatant liquid. Crystallisation of the residue from diethyl ether–light petroleum gave bright yellow *crystals* of (V) (0·18 g, 60%) m.p. 140—141° [Found: C, 27·4; H, 2·3; P, 8·3; *M*, 773 (acetone). $C_{18}H_{18}F_{18}O_6P_2Ni$ requires C, 27·3; H, 2·3; P, 8·3%; *M*, 793], $\nu_{max.}$ (Nujol) 3005vw, 2960w, 2920vw, 2860w, 1657sh, 1652m, 1477vw, 1462w, 1446w, 1412vw, 1337m, 1314m, 1267sh, 1260s, 1243s, 1202s, 1174s, 1141s, 1100sh, 1094m, 1063sh, 1057sh, 1052sh, 1043sh, 1032s, 952w, 943w, 874w, 853vw, 804m, 784m, 765w, 755m, 734m, 723m, 719w, 689m, 666m, and 640m cm^{-1}; ^1H n.m.r. resonance ($CDCl_3$) at τ 6·29 (apparent t, 18H, POCH_3, $|J|$(POCH) 6·0 Hz); ^{19}F n.m.r. resonances ($CDCl_3$) at 56·5 p.p.m. [q, 6F, $CF_3^{(1)}$, *J*(FF) 7 Hz], 57·32 [m, 6F, $CF_3^{(3)}$] and 65·16 [m, 6F, $CF_3^{(2)}$]. Double irradiation of the high field signal reduced the low field signal to a singlet, and the other signal to a triplet [*J*(PF) 11 Hz].

Reaction of hexafluorobut-2-yne (3 mmol) with hexakis(trifluoromethyl)benzenetetrakis(trimethyl phosphite)dinickel (0·3 g, 0·27 mmol) in toluene (15 ml) under identical conditions also gave hexakis(trifluoromethyl)benzene (0·15 g, 0·31 mmol) and (V) (0·12 g, 27%).

Reaction of Complex (I) *with Hexafluorobut-2-yne.*—An excess of hexafluorobut-2-yne (7 mmol) was condensed into a Carius tube (100 ml) containing a toluene solution (15 ml) of (I) (1·0 g, 1·1 mmol). The tube was sealed and heated (75 °C) for 3 days. On cooling a white solid was deposited, which was collected and identified (i.r. and n.m.r.) as hexakis(trifluoromethyl)benzene (0·35 g). Removal of the solvent *in vacuo* gave a golden coloured oil from which an unidentified colourless oil was evaporated on to a cold probe (80 °C, 0·01 mmHg). The residue was chromatographed on a Florisil packed column. Elution with light petroleum gave a yellow fraction, which was fractionally crystallised from light petroleum to give white crystals of (VI) (0·175 g, 30%) and yellow *crystals* of (VII) (0·095 g, 11%) m.p. 80° (Found: C, 27·1; H, 2·0; P, 3·8; F, 43·0. $C_{18}H_{15}F_{18}PPt$ requires C, 27·1; H, 1·9; P, 3·9; F, 42·8%), $\nu_{max.}$ (Nujol) 1625m, 1620sh, 1328m, 1300m, 1270sh, 1255s, 1234s, 1205sh, 1196s, 1170vs, 1155vs, 1128s, 1107m, 1040m, 985w, 946w, 872w, 769m, 746w, 735w, 723w, and 693m cm^{-1}; ^1H n.m.r. resonances ($CDCl_3$) at τ 7·83 (m, 6H, P$CH_2$$CH_3$) and 8·85 (m, 9H, P$CH_2$$CH_3$); $^{19}F\{^{195}Pt\}$ INDOR (CH_2Cl_2), δ_{Pt} −1275 p.p.m. [*J*(PPt) 4001 Hz]; ^{19}F n.m.r. resonances ($CDCl_3$) at 55·5 p.p.m. [m with ^{195}Pt satellites, 6F, $CF_3^{(3)}$, *J*(PF) < 3 Hz, *J*(FPt) 65 Hz], 58·7 [q with ^{195}Pt satellites, 6F, $CF_3^{(1)}$, *J*(FPt) 61 Hz, $J(F^1F^2)$ 10 Hz] and 63·1 [m 6F, $CF_3^{(2)}$]. Double irradiation of the signal at 63·1 p.p.m. reduced the other two signals to singlets with ^{195}Pt satellites.

Reaction of Complex (VI) *with Hexafluorobut-2-yne.*—A toluene solution (10 ml) of (VI) (1·1 g, 1·8 mmol) and hexafluorobut-2-yne (10·0 mmol) contained in a Carius tube (50 ml) was heated (90 °C) for 24 h. On cooling a white solid was precipitated, and was identified as hexakis(trifluoromethyl)benzene. Removal of the solvent *in vacuo* and chromatography of the light petroleum soluble fraction gave on elution with light petroleum–diethyl ether (9 : 1) a yellow fraction. Careful crystallisation (−5 °C) from light petroleum–diethyl ether gave white and yellow crystals, which were separated by hand. The white crystals were identified (i.r. and n.m.r.) as complex (VI) and the yellow crystals as complex (VII).

Reaction of Complex (VII) *with* 1,2-*Bisdiphenylphosphinoethane.*—A solution of (VII) (0·145 g, 0·18 mmol) and diphos (0·8 g, 0·2 mmol) in toluene (10 ml) was refluxed in a nitrogen atmosphere for 1/2 h. Solvent was removed *in vacuo* and the residue recrystallised from methylene chloride–light petroleum to give yellow *crystals* of (VIII) (0·15 g, 80%), m.p. 285° (Found: C, 42·6; H, 2·2. $C_{38}H_{24}F_{18}P_2Pt$ requires C, 42·3; H, 2·2). From $^{19}F\{^{195}Pt\}$ INDOR (CH_2Cl_2) δ_{Pt} −901 p.p.m. [*J*(PPt) 2305 Hz]; ^{19}F n.m.r. (CH_2Cl_2) resonances at 55·0 p.p.m. [q with ^{195}Pt satellites, 6F, $CF_3^{(1)}$, *J*(PtF) 39 Hz, $J(F^1F^2)$ 9 Hz], 56·5 [m with ^{195}Pt satellites, 6F, $CF_3^{(3)}$, *J*(PF) 10 Hz, *J*(PtF) 53 Hz] and 65·2 [m, 6F, $CF_3^{(2)}$]. Double irradiation of the signal at 65·2 p.p.m. reduced the signal at 55·0 p.p.m. to a singlet (with ^{195}Pt satellites) and the signal at 56·5 p.p.m. to a triplet [*J*(PF) 10 Hz] with ^{195}Pt satellites.

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