Fluorinated Alkoxides. Part VIII. Mixed Ligand Complexes of Perfluoropinacol with Ni²⁺, Pd²⁺, Pt²⁺ and Cu²⁺. Solvation Equilibria between 4- and 5-coordinate Ni²⁺

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Perfluoropinacol, $(CF_3)_2C(OH)C(OH)(CF_3)_2$, ionizes by loss of two protons, and the resulting dinegative ion (PFP^{2-}) chelates to Ni^{2+} , Pd^{2+} , Pt^{2+} , and Cu^{2+} . A variety of stable neutral complexes may be isolated if the tetracoordination of the metal ion is completed with two monodentate or one bidentate nitrogen- or phosphorus-containing ligands; square-planar structures are invariably found. The structures of these complexes are contrasted with those of analogous halides, and it is concluded that electronic effects are predominant in determining them, although steric influences may'sometimes be important. The ligand field strength of the perfluoropinacolato ion is approximately equal to that of the thiocyanate ion.

The nickel complexes $Ni(PFP)z^{2-}$ and $(PFP)Ni(RNHCH_2CH_2NHR)$ react with donor solvents (water, methanol, pyridine, etc.) to give equilibria between four- and five-coordinate solvated species; six-coordinate species are not observed. This unusual behavior is attributed to the steric hindrance imposed by the bulk of the PFP^{2-} ligand.

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Le perfluoropinacol, $(CF_3)_2C(OH)C(OH)(CF_3)_2$, s'ionise par perte de deux protons et l'ion dinégatif qui en résulte (PFP^{2-}) se chélate au Ni²⁺, au Pd²⁺, au Pt²⁺ et au Cu²⁺. On peut isoler une variété de complexes neutres stables si la tétracoordination de l'ion métallique est complétée par deux ligands monodentates ou un ligand bidentate contenant de l'azote ou du phosphore; on trouve invariablement des structures plan-carré. Les structures de ces complexes sont en opposition avec celles des halogénures analogues et on en conclut que les effets électroniques sont prédominants dans leur détermination quoique des influences stériques peuvent quelquefois être importantes. La force du champ de ligand des ions perfluoropinacolato est approximativement égale à celle de l'ion thiocyanate.

Les complexes de nickel Ni(PFP)₂²⁻ et (PFP)Ni(RNHCH₂CH₂NHR) réagissent avec des solvants donneurs (eau, méthanol, pyridine etc.) pour conduire à des équilibres entre des espèces solvatées et tétra ou pentacoordonnées; on n'observe aucune espèce hexacoordonnée. On attribue cette attitude anormale à des facteurs stériques imposés par la grosseur du ligand PFP²⁻. [Traduit par le journal]

We have previously demonstrated the value of perfluoropinacol, HOC(CF₃)₂C(CF₃)₂OH (H₂-PFP),¹ as a ligand to first-row transition metals (1). Because of the acidity of the two protons, resulting from the fluorination of the molecule, perfluoropinacol coordinates to transition metal ions as the chelating dianion, $[OC(CF_3)_2O]^2^-$ (PFP²⁻), and stable complexes of Al³⁺, VO²⁺, CrO³⁺, Mn³⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺ have been prepared by reaction in solution and isolated. An analogous chelate is the oxalate ion, and the complexes $[Fe(C_2O_4)_3]^{3-}$ and $[Fe(PFP)_3]^{3-}$ appear to be similar. However, the coordination of oxalate is complicated by the possible bidentate mode of attachment of each carboxylate group, so the PFP dianion

offers a useful example of an unambiguously bidentate, dinegative ligand. The resemblance between a fluorinated ligand and a halide ion has been noted elsewhere (2) and we find many similarities between the complexes formed by PFP^{2-} and those formed by a pair of chloride ions. This approach, in fact, is probably more useful than the formalism of comparing PFP^{2-} derivatives with alkoxides, since the fluorination of the alcohol confers on H_2PFP properties quite different from those of an unfluorinated alcohol. Our aim has therefore been to prepare a number of metal complexes of PFP^{2-} and compare their properties with analogous halide derivatives.

Those complexes which we have previously reported have been anionic species containing two or three PFP^{2-} ions. In the present work, we describe some neutral mixed ligand complexes in which one PFP^{2-} chelate and one or more

¹Throughout this paper, we abbreviate the name of this compound to H_2PFP and its dianion to PFP^{2-} .

neutral ligands are attached to a dipositive metal ion. Many of these are compounds of nickel, where the extensive known chemistry of analogous halide derivatives has shown the possibility of various geometries of coordination for this element. We have also studied some PFP^{2-} complexes of copper(II), palladium(II), and platinum(II).

Previous work on nickel(II) has demonstrated the existence of complexes with octahedral, square planar, and tetrahedral geometries. The last description has been generally applied to a class of nonplanar, four-coordinate, paramagnetic species, even when the structure departs from strictly tetrahedral symmetry; we shall follow that practice. The tetrahalo-ions $[NiX_4]^{2-1}$ (X = Cl, Br, I) are tetrahedral, whereas the phosphine-halo complexes (R₃P)₂NiX₂ are generally trans-square planar for trialkylphosphines and tetrahedral for triarylphosphines. With mixed alkyl-aryl phosphines, e.g. $C_2H_5P(C_6H_5)_2$, either or both geometries may be found, depending on the halide used and the conditions of reaction. Bidentate phosphines give cis-square planar structures.

The different geometries of coordination found in these compounds may be rationalized on either steric or electronic grounds, noting that the ligands of higher ligand field strength favor the square planar configuration in a d⁸ system, and most workers have concluded that the latter effect is dominant. Although the bulkier phosphine ligands produce the tetrahedral configurations, the structures suggest that the greater degree of steric interaction is between the two halide ions. In $[(C_6H_5)_3P]_2NiCl_2$, for example, the P-Ni-P angle is 117°, while the Cl-Ni-Cl angle is 123° (3); the corresponding angles in [(C₆H₅)₃P]₂NiBr₂ are 110 and 126° (4). PFP^{2-} is a bulky ligand overall, but it should take up less space in the immediate coordination sphere of nickel than does a pair of halide ions. The O-Ni-O angle in the chelate ring of the square planar complex $[Ni(PFP)_2]^2$ has been found to be 91° (5), so one might expect, on steric grounds, that a square planar configuration would be more likely for a phosphine-PFP nickel complex than for a phosphine-halo complex, even though a cis-configuration is imposed on the phosphines in the former.

We have therefore prepared a series of phosphine-PFP complexes of nickel and examined their properties. Compounds isolated were $[(C_2H_5)_3P]_2Ni(PFP), [(CH_3)_2P(C_6H_5)]_2Ni-(PFP), [CH_3P(C_6H_5)_2]_2Ni(PFP), [(C_6H_5)_3P]_2-Ni(PFP), and (diphos)Ni(PFP) (diphos = 1,2-bis(diphenylphosphino)ethane). All five of these complexes are yellow-orange and diamagnetic, from which we conclude that they all have a$ *cis*-square planar configuration. A comparison of their electronic spectra in the solid state and in solution (Table 1) shows essentially no difference between the two, indicating that there is no appreciable interaction between molecules in the solid state; the bulky nature of the ligands would, of course, be expected to preclude polymerization.

The availability of structurally similar complexes of halide ions and PFP^2 enables us to compare the ligand field strengths of these anions. For the square planar complexes $[(C_2H_5)_3P]_2NiX_2$, the first transition is found at

TABLE 1. Visible spectra

Compound	Absorption maxima $(cm^{-1})(\varepsilon)^*$				
K ₂ Ni(PFP) ₂	18200; 15600 (sh) (d.r.)				
$[P(C_2H_5)_3]_2Ni(PFP)$	21800 (d.r.)				
	21800 (254) (m)				
	21800 (230) (b)				
$[C_6H_5P(CH_3)_2]_2Ni(PFP)$	22000 (d.r.)				
	21800 (263) (m)				
	22000 (302) (b)				
$[(C_6H_5)_2PCH_3]_2Ni(PFP)$	21600 (d.r.)				
	21500 (270) (m)				
	21600 (316) (b)				
$[(C_6H_5)_3P]_2Ni(PFP)$	21000 (d.r.)				
	21000 (274) (b)				
[diphos]Ni(PFP)	22400 (d.r.)				
	22500 (298) (m)				
	22700 (314) (b)				
[TMED]Ni(PFP)	20400 (d.r.)				
	20000 (75) (m)				
[TEED]Ni(PFP)	19400 (d.r.)				
	19400 (70) (m)				
[bipy]Ni(PFP)	24000 (d.r.)				
LIL	25600 (1640) (m)				
[dibenzen]Ni(PFP)	20000 (54) (d)				
[diethen]Ni(PFP)	19900 (46) (d)				
[DETA]NI(PFP)	11900; 12800; 15700;				
	21500; 26300 (0.r.)				
	12800(13); 11900(12);				
	12000 (10); 13700 (20); 21200 (ch); 26200 (65) (m)				
TMEDICy/DED)	21200 (SII); 20200 (03) (III)				
[IMED]Cu(FFF)	10/00 (d.r.) 17000 (68) (m)				
	18200 (63) (d)				
	16400 (0.5) (0.5				
[IEED]Cu(FFF)	18000 (0.1.)				
	18000 (50) (III)				
	(u) (ec) 0001				

sh = shoulder, d.r. = diffuse reflectance, Solvents: m = methanol, b = benzene, d = dichloromethane.

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the following wavelengths: I^- at 610 nm, Br^- at 542 nm, CI^- at 490 nm, SCN^- at 450–525 nm, and $PFP^{2-}/2$ at 460 nm.

We therefore place PFP^{2-} approximately equal to SCN⁻ in the spectrochemical series, with a greater ligand field strength than the halide ions, and observations on other PFP^{2-} derivatives are consistent with this assessment (6). The square planar geometry of the PFP^{2-} derivatives of nickel(II) is therefore entirely consistent with the greater ligand field strength, as compared with halide ions, so we cannot distinguish between steric and electronic effects in this series.

In an attempt to elucidate this point further, we have prepared nickel(II) complexes with PFP^{2-} and nitrogen donors. Unidentate bases such as pyridine or triethylamine were found to be unsuitable for the preparation of neutral complexes of the type $(R_3N)_2Ni(PFP)$, giving instead ionic salts $[R_3NH^+]_2[Ni(PFP)_2^{2-}]$. However, the use of tetra-*N*-alkyl substituted diamines such as tetramethylethylenediamine (TMED) or tetraethylethylenediamine (TEED) gave the desired complexes (TMED)Ni(PFP) and (TEED)Ni(PFP). As with the phosphine complexes, these were diamagnetic, and we therefore assume them to be *cis*-square planar, both in the solid and in solution.

In comparing these with the corresponding dihalide complexes, the position is more complicated than was the case for the phosphine complexes, since octahedral geometry occurs. (TMED)NiCl₂ contains octahedrally coordinated nickel in the solid state, presumably through bridging halide ions, and an octahedral-tetrahedral equilibrium exists in solution (7). The dibromide and di-iodide are exclusively tetrahedral, while the thiocyanate complex (TMED)- $Ni(NCS)_2$ is insoluble and octahedral with bridging-NCS groups. It would seem likely that the occurrence of tetrahedral geometry in monomeric (TMED)NiCl₂ is the result of electronic, rather than steric, factors, since the metal readily increases its coordination to six by association of the complex, and the change to square planar coordination when PFP²⁻ replaces two Cl⁻ is consistent with the greater ligand field strength of the former. This view is confirmed by the persistence of square planar geometry in PFP²⁻ complexes when TMED is replaced by TEED or the even bulkier ligand [C₆H₅CH₂(CH₃)- $NCH_2 -]_2$.

The ligand 2,2'-bipyridyl (bipy) forms a series of complexes with nickel halides, with the nickel ion being uniformly six-coordinate. The compound (bipy)₂NiCl₂ is a monomeric nonelectrolyte (8), while (bipy)NiCl₂ is polymeric and octahedral through halide bridging (9); the corresponding bromides are similar (10). By contrast, we find the complex (bipy)Ni(PFP) to be monomeric and diamagnetic, and hence presumably square planar. It does not take up additional ligand to give (bipy), Ni(PFP), nor does it form an octahedral dihydrate, as does (bipy)- $NiCl_2$ (11). These results would be expected from the overall bulk of the PFP²⁻ ligand, which would tend to disfavor six-coordinate species. As for the configuration at the nickel atom in the four-coordinate complex, studies on many systems containing aromatic nitrogen donors and halide ions have shown a very fine balance between tetrahedral and square planar structures (12). Although the occurrence of the latter in (bipy)Ni(PFP) is entirely consistent with the greater ligand field strength of PFP^{2-} , the dominant effects here are probably the steric requirements of the chelating bipyridyl and PFP²⁻ rings.

Our general conclusion from a study of the nickel complexes formed by PFP^{2-} is that electronic effects make the more important contribution to determining whether 4-coordinate species adopt a tetrahedral or square-planar conformation. However, the bulk of the PFP^{2-} ligand effectively prevents the formation of a one-atom bridge between two metal ions (as commonly happens with halide ions), so the ready formation of complexes of six-coordinate nickel is prevented.

Solvation Effects and Five-coordinate Nickel

In the solid state, the nickel complexes of PFP^{2-} discussed above were invariably fourcoordinate and square planar, but in several cases a change in the coordination number of the nickel through interaction with the solvent occurred in solution. For example, $K_2Ni(PFP)_2$, a purple solid, gave a yellow solution in water but purple solutions in dry methanol or ether; the latter became yellow on the addition of water. The visible spectra (Fig. 1) showed that the latter color was associated with the development of a strong absorption peak near 400 nm. By contrast, the red complex (TMED)Ni(PFP) showed no color change in a variety of solvents, suggest-

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FIG. 1. Visible absorption spectrum of $K_2Ni(PFP)_2$ in (i) anhydrous ether, (ii) ether containing 1% water.

ing that the bulky tetra-*N*-alkylated ligand was preventing solvation.

Since the neutral diamine-PFP²⁻ complexes of nickel have favorable solubilities and are considerably more stable in solution than Ni- $(PFP)_2^{2-}$ (which is decomposed by basic solvents), we prepared complexes using some N, N'disubstituted diamines, in the hope that they would be less hindered and suitable for a study of solvation effects. The diamines N, N'-diethylethylenediamine (diethen) and N,N'-dibenzylethylenediamine (dibenzen) proved satisfactory, giving the complexes (diethen)Ni(PFP) and (dibenzen)Ni(PFP) as red diamagnetic solids giving red solutions in dichloromethane whose visible spectra showed a single absorption peak near 500 nm, very similar to those of the compounds (TMED)Ni(PFP) and (TEED)Ni(PFP). However, in the presence of coordinating solvents such as water, pyridine, or dimethylformamide (DMF), the solutions became green in color and the spectra changed, with the appearance of a peak at 370-390 nm. Spectra recorded in a range of solvent mixtures (Figs. 2 and 3) showed two isosbestic points, indicating that only two species were present. Pronounced thermochroic behavior was also shown, e.g., the DMF solution of (dibenzen)Ni(PFP), reddish-brown at 25°, became bright green on cooling, while a methanolic solution, containing sufficient water to produce a green color at 25°, reverted to red on heating. A purple solution of $K_2Ni(PFP)_2$ in anhydrous methanol became yellow on cooling to -80° .

Although the majority of square planar nickel(II) complexes become six-coordinate if they undergo solvation, the appearance of these



FIG. 2. Visible absorption spectra of (dibenzen)Ni-(PFP) in water/methanol mixtures.



FIG. 3. Visible absorption spectra of (dibenzen)Ni-(PFP) in pyridine/dichloromethane mixtures.

spectra suggested that, in this case, we were observing five-coordination. In support of this, we estimated the ratio of solvated to unsolvated species in mixed solvent from optical densities, and found this to be directly proportional to the concentration of donor solvent, as would be expected from an equilibrium of the type

 $(dibenzen)Ni(PFP) + L \rightleftharpoons (dibenzen)NiL(PFP)$

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The formation of the solvated complex is, in each case, favored by a decrease in temperature. As additional support for our suggestion that these solutions contain five-coordinate nickel, we prepared a neutral complex of Ni²⁺ with PFP²⁻ and the tridentate ligand diethylenetriamine, NH₂CH₂CH₂NHCH₂CH₂NH₂ (DETA). The product, (DETA)Ni(PFP), was a stable green solid, differing from the complexes prepared previously by being paramagnetic ($\mu_{eff} = 3.14$ B.M.). It was a nonelectrolyte in methanol solution, eliminating the possibility that it could be the ionic compound $[Ni(DETA)_2]^{2+}[Ni (PFP)_2$ ^{2⁻}, and its visible spectrum was very similar to those of our postulated five-coordinate solvates, and also to those of such well-characterized five-coordinate species as ClNiN[CH2CH2- $N(CH_3)_2]_3 \cdot Cl$ (13). We therefore conclude that (DETA)Ni(PFP) is a monomeric species containing five-coordinate, highspin, nickel(II), whereas the analogous halide complexes (DETA)- NiX_2 (X = Cl⁻, Br⁻), are dimeric through halide bridging and contain octahedral nickel (14).

The visible spectrum of (diethen)Ni(PFP) in dichloromethane solution containing benzylamine was very similar to that of (DETA)Ni-(PFP), apart from a residual peak at 500 nm due to remaining four-coordinate species, supporting our suggestion that they are structurally alike.

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The behavior of (diethen)Ni(PFP) and (dibenzen)Ni(PFP) in solution shows that they form five-coordinate 1:1 adducts with a wide variety of ligands. Ready addition occurs with good donors (water, pyridine, primary amines), which interact strongly even in low concentration, while poorer donors (methanol, ether, DMF) only give adducts in high concentrations or at low temperatures. Bulkier ligands (tertiary amines or phosphines) show no sign of interaction. Within the limitations imposed by its stability, the behavior of $Ni(PFP)_2^{2-}$ is similar. The restriction of solvation to a single molecule of ligand is clearly due to the bulk of the PFP²⁻ ion. Examination of molecular models shows that a distortion of the planar arrangement, which would be expected to accompany the attachment of one solvent molecule, produces a conformation of the PFP²⁻ ligand in which the CF₃ groups offer considerable hindrance to the sixth coordination site. However, it is surprising that there is insufficient room even for a second molecule of water, and this appears to be the first reported example of an equilibrium between square-

planar and five-coordinate geometry for nickel associated with the addition of one water molecule.

In previous work, an equilibrium involving five coordination has been seen in the addition of pyridine to the square-planar bis(diethyldithiophosphato)nickel (15), but that system was also in equilibrium with the octahedral complex formed by the addition of a second pyridine molecule. In our studies so far, we have not seen any evidence for a six-coordinate species. It is hoped that additional information on these novel equilibria will be obtained from quantitative studies now in progress.

Copper Complexes

In the synthesis of neutral PFP²⁻ complexes of copper(II), we found N-alkyl substituted ethylenediamines to be the most useful co-ligands, and the complexes (TMED)Cu(PFP) and (TEED)Cu-(PFP) were prepared. On the basis of their visible absorption spectra (Table 1), we suggest a squareplanar configuration for these compounds. Both showed a single, broad, absorption near 550 nm with $\varepsilon \approx 60$. The spectrum did not alter when the solvent was changed from dichloromethane to methanol, showing that the latter was not coordinating to the metal.

The analogous halogen complexes (TMED)-CuCl₂ and (TMED)CuBr₂ have similar absorption spectra with peaks at 700 nm ($\varepsilon = 144$) and 752 nm (265), respectively (C₂H₄Cl₂ solution) (16), which the authors consider to be consistent with an essentially planar structure, and the shift to higher energy in the position of the absorption with PFP²⁻ complexes is consistent with the greater ligand field strength of this ligand in a similar structure. However, this evidence is not strong enough to preclude some distortion from a planar configuration in the PFP²⁻ derivatives.

Palladium and Platinum Complexes

The PFP²⁻ ligand is obviously a "hard" base, in view of its structure and its ready coordination to such hard acids as Fe³⁺, Al³⁺, VO²⁺, and CrO^{3+} . It would therefore be expected to show a lesser tendency to complex with the softer acids Pd^{2+} and Pt^{2+} , and our experiments have confirmed this. We were unable to prepare the anionic complexes $[Pd(PFP)_2]^{2-}$ or $[Pt(PFP)_2]^{2-}$ under conditions where Ni²⁺ readily reacted. However, the mixed ligand phosphine complexes

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Compound	Formula	Carbon		Hydi	Hydrogen		Fluorine		Other	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
K2[Ni(PFP)2] Ni(en)(PFP)	$C_{12}F_{24}O_4K_2Ni$ $C_8H_8F_{12}N_2O_2Ni$	18.0 21.3	17.6 21.2	1.8	0.2 2.3	56.9 50.6	56.7 50.2	Ni: 7.3 Ni: 13.0	7.3 12.8	
Ni(TMED)(PFP)	$C_{12}H_{16}F_{12}N_2O_2Ni$	28.9	28.7	2.9	3.2			Ni: 11.5 N: 6.2	11.6 5.5	
Ni(TEED)(PFP)	$C_{16}H_{24}F_{12}N_2O_2Ni$	34.1	34.8	4.3	4.7	40.5	41.6	Ni: 10.4 N: 5.0	10.4 5.0	
Ni(bipy)(PFP)	$C_{16}H_8F_{12}N_2O_2Ni$	35.1	35.0	1.5	1.7	41.7	41.8	Ni: 10.7	10.8	
Ni(DETA)(PFP)	$C_{10}H_{13}F_{12}N_2O_2Ni$	24.3	24.2	2.6	3.0	46.1	46.3	Ni: 11.9	12.1	
$Ni[(C_2H_5)_3P]_2(PFP)$	$C_{18}H_{30}F_{12}O_2P_2Ni$	34.1	34.5	4.9	4.8	39.5	36.4	Ni: 9.6 P: 9.7	9.4 9.9	
$Ni[(CH_3)_2(C_6H_5)P]_2(PFP)$	C22H22F12O2P2Ni	39.6	39.5	3.3	3.4	34.2	34.4			
$Ni[CH_3(C_6H_5)_2P]_2(PFP)$	$C_{32}H_{26}F_{12}O_2P_2Ni$	48.6	48.4	3.3	3.5					
$Ni[(C_6H_5)_3P]_2(PFP)$	$C_{42}H_{30}F_{12}O_2P_2Ni$	55.1	55.0	3.3	3.4	24.9	25.2			
Ni(diphos)(PFP)	$C_{32}H_{24}F_{12}O_2P_2Ni$	48.7	47.9	3.0	3.6	28.9	30.7			
$Pd[(CH_3)_2(C_6H_5)P]_2(PFP)$	$C_{22}H_{22}F_{12}O_{2}P_{2}Pd$	37.0	36.7	3.1	2.9	31.9	31.9			
$Pt[(CH_3)_2(C_6H_5)P]_2(PFP)$	C ₂₂ H ₂₂ F ₁₂ O ₂ P ₂ Pt	32.9	32.4	2.8	3.0	28.4	28.6			
Cs ₂ [Cu(PFP) ₂]	C ₁₂ F ₂₄ O ₄ Cs ₂ Cu	14.5	14.5	_	0.6	45.9	45.6			
Cu(TMED)(PFP)	C12H16F12N2O2Cu	28.2	28.0	3.1	3.3	44.6	44.5	Cu: 12.4	12.3	
Cu(TEED)(PFP)	$C_{16}H_{24}F_{12}N_2O_2Cu$	33.9	33.9	4.2	4.3	40.2	40.4	Cu: 11.2	11.3	

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 $[(CH_3)_2PC_6H_5]_2M(PFP)$ (M = Pt, Pd) were readily prepared from H_2PFP and the phosphino-dichlorides.

A number of analogous complexes of Pd²⁺ and Pt²⁺ have been reported, in fact the fluorinated derivatives of these metals are more numerous than their hydrocarbon analogs, where alkoxides are uncommon (17). Reaction of zerovalent metal complexes L₄M with hexafluoroacetone gives the 3-membered ring complexes $L_2\dot{MOC}(CF_3)_2$, which undergo further reaction in some cases (depending on the nature of L and M) with a second molecule of ketone to give $L_2MOC(CF_3)_2OC(CF_3)_2$ (18, 19). The palladium(II) complex $[(C_2H_5)_3P]_2Pd(PFP)$ has been prepared by the reaction of $[(C_2H_5)_3P]_2Pd$ - $(CH_3)_2$ with H₂PFP (19), while platinum forms the unusual complex $[(C_6H_5)_3P]_2$ PtOC(CF₃)₂O, a derivative of hexafluoropropane-2,2-diol containing a four-membered chelate ring (20).

Our preparation of a stable PFP^{2-} complex of platinum demonstrates that this system is capable of existence. The fact that it is not formed in the reaction of low-valency metal complexes with hexafluoroacetone, whereas the reduction of the ketone with alkali metals (21), triethyl phosphite (22), or 2-propanol (23) leads readily to the formation of the C—C bond, has been rationalized by Stone (18) in terms of "head-to-tail" dimerization of two molecules of ketone coordinated to the same transition metal atom.

Experimental

General

Volatile compounds were handled in a conventional vacuum system. Infrared spectra were recorded on a Beckman IR-10 instrument; u.v.-visible spectra on Beckman DK or Cary 14 instruments. Microanalyses (Table 2) were performed by Alfred Bernhardt Laboratories, West Germany.

Perfluoropinacol

Caution: attention should be given to the toxic nature of this compound (23).

The most suitable method of preparation for large quantities of perfluoropinacol was found to be that based on triethylphosphite as a reducing agent (22). In a typical reaction, triethylphosphite (125 g, 0.75 mol) was cooled to 0° C and gaseous hexafluoroacetone passed in with constant stirring, until the weight gain indicated uptake of the stoichiometric amount (1.50 mol), over a period of about 2 h.

To the resulting phosphorane was slowly added concentrated sulfuric acid (90 ml), followed by water (90 ml), stirring throughout. The solution was heated under reflux for 2 h to complete hydrolysis, then a further 50 ml of sulfuric acid added. The cooled mixture was repeatedly extracted with dichloromethane, the extract dried (MgSO₄), and fractionally distilled to yield crude perfluoropinacol, b.p. 110–130 °C. The product was redistilled from concentrated sulfuric acid to give anhydrous perfluoropinacol (215 g, 0.64 mol, 85% yield, b.p. 129–130 °C, m.p. 28–29 °C).

Nickel Complexes

The same general route was employed for the majority of the mixed-ligand Ni-PFP complexes. In a typical experiment, triethylphosphine (2.0 g, 17 mmol) was added slowly under nitrogen to a water-methanol solution of nickel nitrate hexahydrate (2.6 g, 8.9 mmol) and perfluoropinacol (2.8 g, 8.4 mmol). A solution of potassium hydroxide in methanol was then added dropwise with stirring to pH 8, and the resulting orange precipitate recrystallized from methanol/water to give bis(triethylphosphine)perfluoropinacolatonickel(II), m.p. 181°.

The same method gave:

 $[(CH_3)_2P(C_6H_5)]_2Ni(PFP)$, orange, m.p. 132–133°, from methanol/water.

 $[CH_3P(C_6H_5)_2]_2Ni(PFP)$, orange, m.p. 172–173°, from ethanol.

 $[(C_6H_5)_2PCH_2-]_2Ni(PFP)$, golden, m.p. 228°, from methanol/water.

 $[(C_6H_5)_3P]_2$ Ni(PFP). This preparation was carried out in *t*-butyl alcohol and the orange product recrystallized from chloroform/pentane, m.p. 208°.

 $[(C_2H_5O)_3P]_2Ni(PFP)$. This complex could not be prepared directly, but was made by the reaction of excess triethyl phosphite with $K_2Ni(PFP)_2$ in aqueous ethanol, followed by reduction in volume and recrystallization of the precipitated product from dichloromethane/pentane.

(TMED)Ni(PFP), red, m.p. 232°, from methanol. (TEED)Ni(PFP), magenta, m.p. 239-240° (decomp) from methanol.

(bipy)Ni(PFP), orange-brown, m.p. 280° (decomp) from ethanol/water.

The above nine complexes were diamagnetic and each showed a single peak in its ¹⁹F n.m.r. spectrum in the range 70.6–71.3 p.p.m. from CFCl₃.

(DETA)Ni(PFP), green, m.p. $242-245^{\circ}$ (decomp) from methanol. This complex was paramagnetic with $\mu_{eff} = 3.14$ B.M. at 25°. It was a nonelectrolyte in methanol solution.

Palladium and Platinum Complexes

Dichlorobis (dimethylphenylphosphino) palladium (II) (0.30 g, 0.66 mmol) and H₂PFP (0.22 g, 0.66 mmol) were dissolved in methanol, and methanolic potassium hydroxide added to pH 8. The solution was evaporated to dryness and extracted with dichloromethane. Concentration of the extract gave [(CH₃)₂P(C₆H₅)]₂Pd(PFP), off-white, m.p. 157° (decomp).

The platinum analog was similarly prepared; white, m.p. $174-175^{\circ}$.

Copper Complexes

TMED (1.20 g, 10.4 mmol) was slowly added to a solution of copper sulfate pentahydrate (2.0 g, 8.0 mmol) and H₂PFP (2.7 g, 8.1 mmol) in methanol/water, followed by methanolic potassium hydroxide to pH 8. The resulting purple precipitate was recrystallized from

acetone/water to give (TMED)Cu(PFP), m.p. 191–192° (decomp), $\mu_{eff} = 1.87$ B.M./25°.

TEED similarly gave (TEED)Cu(PFP), purple, m.p. 195–197° (decomp), $\mu_{eff} = 1.87$ B.M./25°.

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- M. ALLAN and C. J. WILLIS. J. Am. Chem. Soc. 90, 5343 (1968); C. J. WILLIS. Chem. Commun. 944 (1972); 117 (1974).
- 2. R. NYHOLM. Q. Rev. 24, 1 (1970).
- 3. G. GARTON, D. E. HENN, H. M. POWELL, and L. M. VENANZI. J. Chem. Soc. 3625 (1963).
- J. A. J. JARVIS, R. H. B. MAIS, and P. G. OWSTON. J. Chem. Soc. A, 1473 (1968).
- 5. D. M. BARNHART and E. C. LINGAFELTER. Unpublished results.
- 6. C. J. WILLIS. Unpublished results.
- 7. L. SACCONI and I. BERTINI. Inorg. Nucl. Chem. Lett. 2, 29 (1966).
- C. M. HARRIS and E. D. MCKENZIE. J. Inorg. Nucl. Chem. 19, 372 (1961).
- 9. R. H. LEE, E. GRISWOLD, and J. KLEINBERG. Inorg. Chem. 3, 1278 (1964).

- R. J. H. CLARK and C. S. WILLIAMS. Spectrochim. Acta. 23A, 1055 (1967).
- 11. К. АКАВОRI, Н. МАТSUO, and Y. YAMAMOTO. J. Inorg. Nucl. Chem. 33, 2593 (1971).
- 12. E. UHLIG. Coord. Chem. Rev. 10, 227 (1973).
- 13. M. CIAMPOLINI and N. NARDI. Inorg. Chem. 5, 41 (1966).
- N. F. CURTIS and H. K. J. POWELL. J. Chem. Soc. A, 3069 (1968).
- 15. R. L. CARLIN, J. S. DUBNOFF, and W. T. HUNTRESS, Proc. Chem. Soc. 228 (1964).
- I. BERTINI and F. MANI. Inorg. Chem. 6, 2032 (1967).
 F. R. HARTLEY. The chemistry of platinum and pal-
- ladium. Wiley, New York. 1973. p. 172.
- 18. F. G. A. STONE. Pure Appl. Chem. 30, 551 (1972).
- 19. H. D. EMPSALL, M. GREEN, and F. G. A. STONE. J. Chem. Soc. Dalton, 96 (1972).
- 20. P. J. HAYWARD and C. J. NYMAN. J. Am. Chem. Soc. 93, 617 (1971).
- 21. M. ALLAN, A. F. JANZEN, and C. J. WILLIS. Can. J. Chem. 46, 3671 (1968).
- N. P. GAMBARYAN, YU. A. CHEBURKOV, and I. L. KNUNYANTS. Izv. Akad. Nauk. SSSR, Ser. Khim. 1526 (1964).
- 23. W. J. MIDDLETON and R. V. LINDSEY. J. Am. Chem. Soc. 86, 4948 (1964).

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