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A Triad of Bis(orthometalated) d^8-Complexes Containing Four-Membered Rings

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Reaction of 2-LiC$_6$F$_4$PPh$_2$ with [MCl$_2$(SEt$_2$)$_2$] in diethyl ether gives the monomeric bis(chelate) complexes *trans*-[M(κ^2-2-C$_6$F$_4$PPh$_2$)$_2$] [M = Pt (**1**), Pd (**2**)] or, in the case of platinum, a mixture of *cis*- and *trans*-isomers. Treatment of a mixture of NiCl$_2$ and 2-BrC$_6$F$_4$PPh$_2$ in THF with zinc dust gives *trans*-[Ni(κ^2-2-C$_6$F$_4$PPh$_2$)$_2$] (**3**). The four-membered chelate rings in **1**−**3** are opened on addition of the bidentate ligand 1,2-bis(diphenylphosphino)ethane (dppe), and, in the case of **3**, 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen), to give complexes of the type *cis*-[M(κC-C$_6$F$_4$-2-PPh$_2$)$_2$(L-L)] [L-L = dppe, M = Ni (**6**), Pd (**7**), Pt (**8**); M = Ni, L-L = bipy (**9**), phen (**10**)], in which the PPh$_2$ groups are uncoordinated. Complexes **6**−**8** show unexpectedly large four-bond coupling constants ($^4J_{PF}$), in the range 75−95 Hz, between the fluorine atoms (F^6) *ortho* to the metal−carbon σ-bond and the phosphorus atoms of the PPh$_2$ groups, possibly because F^6 and the lone pairs on phosphorus adopt a close to synperiplanar conformation. Treatment of **2** with [PdCl$_2$(NCMe)$_2$] gives the dinuclear complex [Pd$_2$(μ-Cl)$_2$(κ^2-2-C$_6$F$_4$PPh$_2$)$_2$] (**11**), which dimerizes in solution to the tetranuclear complex [Pd$_4$(μ-Cl)$_4$(μ-2-C$_6$F$_4$PPh$_2$)$_4$] (**12**) as a result of opening of the chelate 2-C$_6$F$_4$PPh$_2$ rings. Carbon monoxide inserts into a nickel−carbon σ-bond of **3** to give, after oxidation, bis-2,2′-(diphenylphosphinoyl)octafluorobenzophenone, {2,2′-C$_6$F$_4$P(O)Ph$_2$}$_2$CO (**14**). The molecular structures of complexes **1**−**3**, **6**, **8**, **9**, and **14** have been determined by single-crystal X-ray methods.

Introduction

Metal complexes of the bidentate carbanion [2-C$_6$H$_4$PPh$_2$]$^-$ are now known for most of the middle and later d-block elements, octahedral (d^6) and planar (d^8) complexes of the 4d- and 5d-series being particularly prevalent. This chemistry has been reviewed in detail recently.[1] The complexes are most often generated by orthometalation (C−H activation) of coordinated triphenylphosphine, though procedures based on transmetalation from 2-LiC$_6$H$_4$PPh$_2$ [for Au(I), Pt(II), and Rh(III)] and on oxidative addition of 2-BrC$_6$H$_4$PPh$_2$ [for Pd(II) and Rh(III)] have also been developed. Similar methods have also been widely employed in the synthesis of five- and six-membered cyclometalated complexes[2−5] and of pincer complexes.[6]

As shown in Figure 1, the ligand [2-C$_6$H$_4$PPh$_2$]$^-$ usually binds as a chelate group ($\kappa^2 P,C$), forming a four-membered ring, but the bridging ($\mu_2 P,C$) mode is also well established, for example, in complexes of digold(I),[7−9] diplatinum(I),[10,11] tetrapalladium(II),[12,13] and dirhodium(II).[14−16] Facile interconversion between these coordination modes has been demonstrated, especially in the case of palladium(II).[12,13]

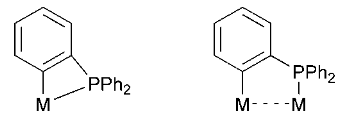

Figure 1. Coordination modes of [2-C$_6$H$_4$PPh$_2$]$^-$.

It is well known that metal-pentafluorophenyl complexes are more stable and numerous than their metal-phenyl counterparts, perhaps because the M−C σ-bond is strengthened by the electronegative fluorine substituents,[17] and an extensive chemistry based on M-C$_6$F$_5$ complexes has been developed.[18,19] We

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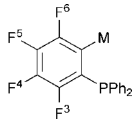
Table 1. Spectroscopic Data for Complexes 1−3 and 6−10[a,b]

complex	δ_F	δ_P
cis-$[Pt(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)_2]$ (*cis*-**1**)[c]	−120.1 (br s, J_{PtF} 164 Hz, F^6), −137.0 (br m, F^3), −149.0 (br m, F^5), −157.7 (t, sep ca. 20 Hz, F^4)	−64.2 (s, J_{PtP} 1697 Hz)
trans-$[Pt(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)_2]$ (*trans*-**1**)[c]	−124.3 (t, sep ca. 26 Hz, J_{PtF} 163 Hz, F^6), −135.2 (td, sep ca. 20 Hz, 4 Hz, F^3), −150.0 (qd, overlapping ^{195}Pt satellites, F^5), −159.1, (t, sep ca. 20 Hz, F^4)	−55.6 (s, J_{PtP} 2264 Hz)
trans-$[Pd(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)_2]$ (**2**)[c]	−122.1 (t of m, sep ca. 26 Hz, F^6), −134.0 (t of m, sep ca. 22 Hz, F^3, −150.0 (qd, sep ca. 30 Hz, 17 Hz, 4 Hz, F^5), −158.7 (approx t, sep ca. 17 Hz, F^4)	−55.2 (s)
trans-$[Ni(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)_2]$ (**3**)[d]	−122.8 (approx t, sep ca. 26 Hz, F^6), −134.6 (approx t, sep ca. 26 Hz, F^3), −150.6 (4 line pattern, F^5), −157.3 (approx t, sep ca. 20 Hz, F^4)	−44.2 (s)
$[Ni(\kappa C\text{-}2\text{-}C_6F_4PPh_2)_2(dppe)]$ (**6**)[d]	−104.1 (d of spt, sep 98 Hz, F^6), −123.8 (approx 1:2:2:1 q, sep 21.3 Hz, 14.7 Hz, 22.9 Hz, F^3), −153.3 (4 line pattern, F^5), −162.4 (approx 1:2:1 t, sep 22 Hz, F^4)	48.7 (t, *J* 11.6 Hz, dppe), −0.1 (dd, *J* 26.8 Hz, 95.5 Hz, PPh_2)
$[Pd(\kappa C\text{-}2\text{-}C_6F_4PPh_2)_2(dppe)]$ (**7**)[d]	−105.2 (overlapping d of spt, F^6), −123.8 (approx 1:2:2:1 q, F^3), −153.3 (5 line pattern, F^5), −162.4 (approx 1:2:1 t, sep 22 Hz, F^4)	44.2 (br t, *J* ca. 14 Hz, dppe), −2.2 (dd, *J* 25.9 Hz, 76.9 Hz, PPh_2)
$[Pt(\kappa C\text{-}2\text{-}C_6F_4PPh_2)_2(dppe)]$ (**8**)[d]	−107.5 (d of m, J_{PtP} 326 Hz, F^6), −123.8 (br m, F^3), −153.3 (approx 1:2:1 t, F^5), −162.9 (approx 1:2:1 t, sep 22 Hz, F^4)	39.8 (br s, J_{PtP} 2137 Hz, dppe), −1.6 (dd, *J* 26.8 Hz, 81.5 Hz, J_{PtP} 227 Hz, PPh_2)
$[Ni(\kappa C\text{-}2\text{-}C_6F_4PPh_2)_2(bipy)]$ (**9**)[e]	−117.8 (spt, F^6), −124.6 (approx 1:2:2:1 q of d, F^3), −155.6 (4d, F^5), −162.3 (t, sep 20.7 Hz, F^4)	−6.1 (m, PPh_2)
$[Ni(\kappa C\text{-}2\text{-}C_6F_4PPh_2)_2(phen)]$ (**10**)[e]	−117.9 (spt, F^6), −124.5 (approx 1:2:2:1 q of d, F^3), −155.6 (4d, F^5), −162.3 (t, sep 21.3 Hz, F^4)	−6.0 (m, PPh_2)

[a] Numbering of fluorine atoms:



[b] Multiplicities reported for complexes *cis*-**1**, *trans*-**1**, and **8** do not include ^{195}Pt satellites. [c] Measured in $CDCl_3$. [d] Measured in C_6D_6. [e] Measured in CD_2Cl_2.

show here that a similar effect operating in $[2\text{-}C_6F_4PPh_2]^-$ allows access to the first series of homoleptic, bis(orthometalated) complexes of the d^8-elements, $[M(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)_2]$ [M = Pt (**1**), Pd (**2**), Ni (**3**)]. In the case of $[2\text{-}C_6H_4PPh_2]^-$, only the platinum(II) bis(chelate) complex, *cis*-$[Pt(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)_2]$ (**4**), is known,[10] and even this is thermodynamically unstable with respect to the dimer $[Pt_2(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$.[11] All attempts to isolate palladium(II) and nickel(II) bis(chelate) complexes of $[2\text{-}C_6H_4PPh_2]^-$ have failed so far. The stabilizing effect of electronegative substituents in the σ-bonded aryl ring has been foreshadowed in the isolation of *trans*-$[Ni(\kappa^2\text{-}2\text{-}C_6Cl_4PEt_2)_2]$ (**5**) from the oxidative addition of $C_6Cl_5PEt_2$ to $[Ni(COD)_2]$.[20,21]

Results

Synthesis of Bis(chelate) Complexes. Treatment of the organolithium reagent $2\text{-}LiC_6F_4PPh_2$[22] with $[PtCl_2(SEt_2)_2]$ gave the colorless bis(chelate) complex $[Pt(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)_2]$ (**1**) as a mixture of *cis*- and *trans*-isomers in ca. 30% yield (*cis/trans* ratio approximately 1:3). The *cis*-isomer was the almost exclusive product, in about 66% yield, starting from $[PtI_2(COD)]$. The *cis*-isomer was converted into the *trans*-isomer when toluene solutions were heated under reflux. The corresponding reaction of $[PdCl_2(SEt_2)_2]$ or $[PdBr_2(COD)]$ with $2\text{-}LiC_6F_4PPh_2$ gave colorless *trans*-$[Pd(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)_2]$ (**2**), in yields of 30−40%. The yellow nickel analogue, *trans*-$[Ni(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)_2]$ (**3**), could not be made similarly from precursors such as $NiCl_2$, $Ni(acac)_2$, or $Ni(OOCCF_3)_2$, but was isolated in 30% yield from zinc dust reduction of a mixture of anhydrous $NiCl_2$ and $2\text{-}BrC_6F_4PPh_2$ in THF. This procedure follows that employed by Sacco et al.[23] for the preparation of the nickel(0) complexes $[Ni(CO)_2(PPh_3)_2]$ and $[Ni(C_2H_4)(PPh_3)_2]$. Complex **3** could also be isolated from the reaction of $2\text{-}BrC_6F_4PPh_2$ with $[Ni(COD)_2]$, but the yield was poor (ca. 10%).

The spectroscopic data for complexes **1**−**3** are collected in Table 1. The ^{31}P NMR spectra consist of a singlet in the region of δ −40 to −65, the shielding being characteristic of phosphorus in four-membered chelate rings.[24] The signals are broad ($W_{1/2}$ ca. 16 Hz), probably owing to unresolved ^{19}F coupling. In addition, the resonances for *cis*- and *trans*-**1** show ^{195}Pt satellites with couplings of 1697 and 2294 Hz, respectively, the magnitudes being typical for phosphorus *trans* to aryl carbon

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(21) Abbreviations: COD = 1,5-cyclooctadiene, C_8H_{12}; dppe = 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$; bipy = 2,2′-bipyridyl, 2,2′-$(C_5H_4N)_2$; phen = 1,10-phenanthroline, $C_{12}H_8N_2$.

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and to phosphorus, respectively; cf. *cis*-[$PtPh_2(PPh_3)_2$] (J_{PtP} 1762 Hz)[25] and *trans*-[$PtCl_2(PPh_3)_2$] (J_{PtP} 2637 Hz).[26]

The ^{19}F NMR spectra of **1**−**3** consist of four multiplets of equal intensity centered at ca. δ −120, −135, −150, and −158, relative to $CFCl_3$, corresponding to the inequivalent fluorine atoms of the 2-$C_6F_4PPh_2$ unit. In the spectra of *cis*- and *trans*-**1**, the resonances at ca. δ −120 show ^{195}Pt satellites (J_{PtF} ca. 164 Hz), indicating that this signal in all three compounds should be assigned to F^6, adjacent to the M−C σ-bond. Similar chemical shifts for $F^{2,6}$ are observed in comparable pentafluorophenylplatinum(II) complexes, though the J_{PtF} values for *cis*- and *trans*-**1** are about half that observed in *cis*-[$Pt(C_6F_5)_2(PPh_3)_2$] (315 Hz)[27] and *cis*-[$Pt(C_6F_5)_2$(dppe)] (309 Hz),[28] presumably because of the presence of the strained four-membered ring. The resonance at ca. δ −135 is assigned to F^3 adjacent to the PPh_2 group, cf. δ −130.6 and −127.7 for the *ortho*-fluorine atoms in $(C_6F_5)_3P$ and $C_6F_5PPh_2$, respectively.[29] Since the resonance at ca. δ −150 in the spectrum of *trans*-**1** shows observable coupling with ^{195}Pt (although the satellites overlap the main multiplet), we assign the signal in this region in all three complexes to F^5, in the remaining position that is *meta* to the M−C σ-bond; the signal at ca. δ −158 is therefore due to F^4, *para* to the M−C σ-bond.

The presence of four-membered chelate rings in **1**−**3** was confirmed by single-crystal X-ray diffraction studies. Crystallization of an isomeric mixture of **1** from dichloromethane/hexane gave crystals of *trans*-**1** as colorless plates (monoclinic, space group $P2_1/c$, form A) and colorless needles (monoclinic, space group $C2/c$, form B) and *cis*-**1** as pale yellow plates (monoclinic, space group $C2/c$); complexes **2** and **3** crystallize in space group $P2_1/c$ and are isomorphous with form A of *trans*-**1**. The molecular structure of *cis*-**1** is shown in Figure 2, and selected bond lengths and angles for *cis*-**1**, *trans*-**1** (both modifications), and **2** are collected in Table 2. The molecular structure of **3** is shown in Figure 3, together with selected bond lengths and angles.

All three complexes show the expected, approximately square-planar coordination about the metal atoms, distorted as a consequence of the narrow bite angle of the chelate groups. The Pt−C distance in *cis*-**1** [2.110(4) Å] is slightly longer than that in the protio analogue *cis*-[$Pt(\kappa^2$-2-$C_6H_4PPh_2)_2$] (**4**) [2.063(2) Å],[10] whereas the Pt−P distances in *cis*-**1** and **4** do not differ significantly [2.2754(9), 2.297(1) Å, respectively]. The C−Pt−C angle in *cis*-**1** [112.3(2)°] is significantly greater than that in **4** [106.3(1)°], while the P−Pt−P angles follow the reverse trend [108.89(5)° in *cis*-**1**, 116.25(3)° in **4**], perhaps to accommodate the larger fluorine substituents. These angles are similar to the corresponding angles in *cis*-[$Pt(\kappa^2$-C_6H_3-6-Me-2-$PPh_2)_2$], in which the bulky methyl substituents are *ortho* to the M−C σ-bonds.[11] The metrical parameters for the two modifications of *trans*-**1** are almost identical. There is also little difference in the metrical parameters of the platinum(II) complex *trans*-**1** and the palladium(II) complex **2**; a marked lengthening of the M−C bonds and shortening of the M−P bond lengths for Pt compared with Pd similar to that found in the isostructural dimethylmetal(II) complexes *cis*-[$M(CH_3)_2(PMePh_2)_2$] (M = Pd, Pt) is not evident.[30,31] The M−C distances in *trans*-**1** and **2** are ca. 0.04 Å less than that in *cis*-**1**, whereas the M−P distances are ca. 0.03 Å longer, reflecting the higher *trans*-influence of the phosphorus donor relative to that of the fluoroaryl carbon. The bite angle of the chelate ligands in *cis*-**1**, *trans*-**1**, and **2** lies within the range 68−69° usually found for orthometalated PPh_3 complexes.[1]

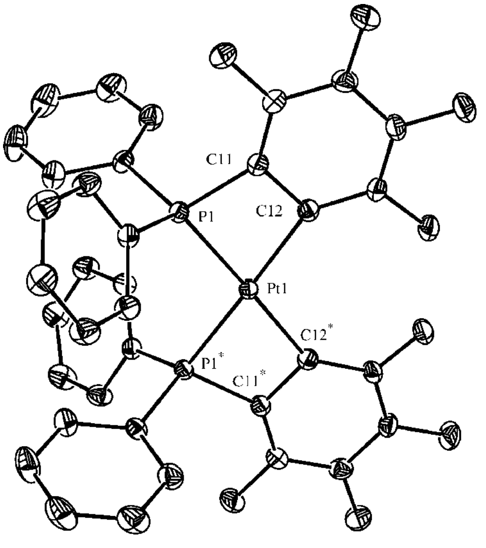

Figure 2. Molecular structure of *cis*-[$Pt(\kappa^2$-2-$C_6F_4PPh_2)_2$], *cis*-**1**. Ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes *cis*-1, *trans*-1, and 2

	cis-**1**	*trans*-**1** (form A)	*trans*-**1** (form B)	**2**
M(1)−P(1)	2.2754(9)	2.2960(6)	2.3025(9)	2.3069(4)
M(1)−C(12)	2.110(4)	2.063(2)	2.074(4)	2.0672(16)
P(1)−M(1)−C(12)	69.42(10)	69.02(6)	69.07(10)	69.39(5)
P(1)−M(1)−C(12*)	178.29(11)	110.98(6)	110.93(10)	110.61(5)
P(1)−M(1)−P(1*)	108.89(5)	180.0	180.0	180.0
C(12)−M(1)−C(12*)	112.3(2)	180.0	180.0	180.0

The Ni−P and Ni−C distances in **3** are similar to those found in *trans*-[$Ni(\kappa^2$-2-$C_6Cl_4PEt_2)_2$] (**5**)[20] and are ca. 0.1−0.15 Å less than the corresponding metal−ligand distances in *trans*-**1** and **2**, corresponding to the smaller size of nickel relative to that of palladium or platinum. This feature may also account for the fact that the bite angle of the ligand has increased to ca. 73°, again similar to that found in **5**.

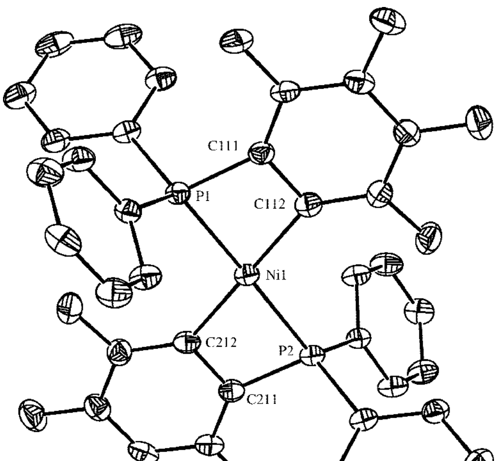

Figure 3. Molecular structure of *trans*-[$Ni(\kappa^2$-2-$C_6F_4PPh_2)_2$], **3**. Ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni(1)−P(1), 2.2035(9), Ni(1)−P(2), 2.2058(9), Ni(1)−C(112) 1.941(3), Ni(1)−C(212) 1.934(3), P(1)−Ni(1)−C(112) 72.76(10), P(2)−Ni(1)−C(212) 72.87(10), P(1)−Ni(1)−C(212) 106.66(10), P(2)−Ni(1)−C(112) 107.67(10), P(1)−Ni(1)−P(2) 177.90(4), C(112)−Ni(1)−C(212) 178.85(14).

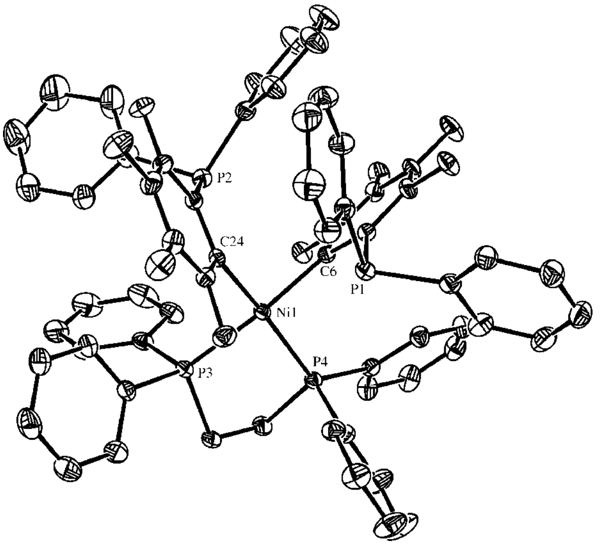

Figure 4. Molecular structure of [Ni(κC-2-$C_6F_4PPh_2$)$_2$(dppe)] **6**. Ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity.

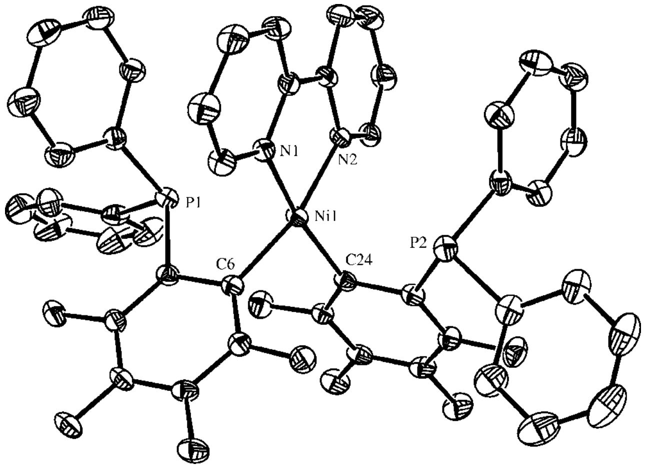

Figure 5. Molecular structure of *cis*-[Ni(κC-2-$C_6F_4PPh_2$)$_2$(bipy)] **9**. Ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni(1)−N(1) 1.9489(19), Ni(1)−N(2) 1.9394(19), Ni(1)−C(6) 1.883(2), Ni(1)−C(24) 1.901(2), N(1)−Ni(1)−C(6) 95.18(9), N(2)−Ni(1)−C(24) 96.99(9), N(1)−Ni(1)−C(24) 166.28(9), N(2)−Ni(1)−C(6) 163.63(9), N(1)−Ni(1)−N(2) 82.79(8), C(6)−Ni(1)−C(24) 88.80(10).

Reactions with Bidentate Ligands. The phosphorus atoms of the four-membered chelate rings in **1**−**3** are displaced by 1,2-bis(diphenylphosphino)ethane to give complexes of the type *cis*-[M(κC-2-$C_6F_4PPh_2$)$_2$(dppe)] [M = Ni (**6**), Pd (**7**), Pt (**8**)]. Similar reactions have been reported for the platinum(II) complex **4**.[32] The phosphorus atoms of the nickel complex **3** are also displaced by the bidentate nitrogen donors 2,2′-bipyridine and 1,10-phenanthroline to give *cis*-[Ni(κC-2-$C_6F_4PPh_2$)$_2$(L-L)] [L-L = bipy (**9**), phen (**10**)] as dark colored solids; the palladium and platinum bis(chelate) complexes **1** and **3** are inert under similar conditions.

The ESI mass spectra of **6**−**10** show the expected parent ion peaks. The structures of the complexes follow from the NMR spectroscopic data, which are discussed below, and from single-crystal X-ray crystallographic analyses of **6**, **8**, and **9**. Compounds **6** and **8** are isomorphous and isostructural (triclinic, space group $P\bar{1}$); **9** is monoclinic ($P2_1/n$). The molecular structures of **6** and **9** are shown in Figures 4 and 5, respectively. Selected bond lengths and angles for **6** and **8** are listed in Table 3; those for **9** are given in the caption to Figure 5.

All three complexes show the expected, close to square-planar coordination geometry about the metal atom. The phosphorus atoms of the 2-$C_6F_4PPh_2$ groups, P(1) and P(2), are not within bonding distance of the metal atoms [Ni···P 3.442(1), 3.444(1) Å in **6**, 2.907(1), 3.048(1) Å in **9**; Pt···P 3.478(1), 3.474(1) Å in **8**]. The Ni−C bond lengths in **6** are similar to those in the parent bis(chelate) complex **3**. The Ni−C bond lengths [1.940(2), 1.950(2) Å] are also similar to those reported for nickel-aryl and nickel-pentafluorophenyl complexes containing tertiary phosphines, e.g., *trans*-[Ni(2-MeC_6H_4)$_2$(PMe_2Ph)$_2$] [1.933(16), 1.950(12) Å (*syn*-isomer), 1.942(3) Å (*anti*-isomer)],[33] *trans*-[Ni(C_6F_5)$_2$($PMePh_2$)$_2$] [1.939(3) Å],[34] [Ni(C_6R_5)(η^5-C_5H_5)(PPh$_3$)] [1.904(7) Å (R = H),[35] 1.914(14) Å (R = F)[36]], and [Ni{κ^2-*C,O*-2-C_6H_4C(=CHMe)O}(^{i}Pr$_2$PCH$_2$CH$_2$P^{i}Pr$_2$)] [1.913(4) Å].[37] The Ni−P distances in **6** of 2.20 Å are unexceptional.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complexes 6 and 8

	[Ni(κC-2-$C_6F_4PPh_2$)$_2$-(dppe)], **6**	[Pt(κC-2-$C_6F_4PPh_2$)$_2$-(dppe)], **8**
M(1)−C(6)	1.940(2)	2.065(3)
M(1)−C(24)	1.950(2)	2.071(2)
M(1)−P(3)	2.1986(6)	2.2629(7)
M(1)−P(4)	2.2078(6)	2.2655(6)
C(6)−M(1)−C(24)	91.30(8)	90.91(9)
C(6)−M(1)−P(4)	92.53(6)	93.10(7)
C(24)−M(1)−P(3)	92.33(6)	92.66(7)
P(3)−M(1)−P(4)	86.35(2)	85.74(2)
C(6)−M(1)−P(3)	166.60(7)	166.68(8)
C(24)−M(1)−P(4)	168.76(7)	169.06(8)

In the isostructural platinum(II) complex **8**, the Pt−C and Pt−P distances are not significantly different from those in the precursor *cis*-**1** and are similar to those in *cis*-[Pt(C_6F_5)$_2$-(dppe)].[28] In the bipy complex **9**, the Ni−C bond lengths are significantly shorter, by 0.04−0.06 Å, than those in the dppe complex **6** but are similar to those in other Ni-C_6F_5 complexes containing N-donors, e.g., [Ni(C_6F_5)$_2$(bipy)] [1.903(4), 1.907(4) Å][38] and [Bu_4N][Ni(C_6F_5)$_2$(2-SC_5H_4N)] [1.891(6), 1.894(6) Å].[39]

The ^{31}P and ^{19}F NMR spectra of compounds **6**−**10** are listed in Table 1. The ^{31}P NMR spectra of **6**−**8** consist of two sets of signals in the region of δ 40 and 0, assignable to coordinated

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dppe and to uncoordinated PPh_2 groups, respectively. The dppe resonance of the nickel complex **6** is a well-resolved triplet with a separation of 11.6 Hz, that of the palladium complex **7** is a poorly resolved triplet (separation ca. 14 Hz), while that of **8** is a broad singlet accompanied by ^{195}Pt satellites (J_{PtP} 2137 Hz). The PPh_2 resonances of **6**−**8** display an unexpected pattern, consisting of a well-resolved doublet of doublets with separations of 26.8, 95.5 Hz (**6**), 25.9, 76.9 Hz (**7**), and 26.5, 81.5 Hz (**8**). In the case of **8** there are also ^{195}Pt satellites (J_{PtP} 227 Hz), somewhat greater than the corresponding values in [Pt(κC-2-$C_6H_4PPh_2$)$_2$(dppe)] (170 Hz).[32] The separations in the doublet of doublets are not reproduced in the dppe resonance; hence the unexpected pattern is not due to coupling with the ^{31}P nuclei of dppe. Likewise, the separations observed in the dppe resonances of **6** and **7** are not reproduced in the corresponding PPh_2 resonances; hence these separations do not arise from coupling with the ^{31}P nuclei of the PPh_2 groups. These conclusions are supported by the failure to observe cross-peaks in the 2D COSY $^{31}P/^{31}P$ NMR spectra. The uncoordinated PPh_2 resonances of **9** and **10**, in contrast with those of **6**−**8**, are in each case the expected singlet at ca. δ −6, with multiplet fine structure, presumably due to ^{19}F coupling.

We thought at first that the doublet of doublets for the PPh_2 groups in **6**−**8** might arise from inequivalence of the PPh_2 groups in solution caused by restricted rotation about the M−$C_6F_4PPh_2$ bonds, even though this would have implied a remarkably large, six-bond P−P coupling constant (ca. 26 Hz). This explanation did not seem implausible given the ample evidence for restricted rotation about M−C_6F_5 bonds[40−49] and for slowed rotation about M−P and P−C bonds in platinum(II) complexes of $(C_6F_5)_3P$.[50−52] However, the frequency separation between the pairs of doublets was found to be the same at 202.3 MHz as at 121.4 MHz; hence there is only one ^{31}P chemical shift and the observed pattern can only be due to P−F coupling.

The ^{19}F NMR spectra of **6**−**10** consist of the expected four multiplets whose chemical shifts and assignments are similar to those of their chelate precursors (Table 1). In each case, the main difference from the spectra of **1**−**3** is that the resonance due to F^6 is shifted to higher frequency (δ_F ca. −105 in **6**−**8**, ca. −117 in **9** and **10**) and in the case of **6**−**8** appears as a doublet of multiplets. In the platinum(II) complex **8**, the coupling constant of ^{195}Pt to F^6 (326 Hz) is approximately double that in the precursor **1** and is similar to the values reported for coupling to the *ortho*-fluorine atoms in *cis*-$[Pt(C_6F_5)_2(PPh_3)_2]$[27] and $[Pt(C_6F_5)_2(dppe)]$[28] (see above). A $^{31}P/^{19}F$ heteronuclear multiple quantum correlation (HMQC) experiment on the palladium complex **7** showed well-defined cross-peaks associated with the resonances at δ_F −105.2 (F^6) and −123.8 (F^3); the coupling constants are ca. 75 and 25 Hz, respectively, in reasonable agreement with the separations observed in the 1D ^{31}P NMR spectrum. A similar experiment on the nickel(II)-bipy complex **9** also showed cross-peaks for the resonances at δ_F −117.8 (F^6) and −124.6 (F^3), but the coupling to F^6 (ca. 30 Hz) is clearly less than that in the dppe complex; the coupling to F^3 is less than 20 Hz. In the 1D ^{19}F NMR spectrum of the nickel-dppe complex **6**, the doublet of multiplets due to F^6 is so well resolved that the coupling with phosphorus can be read off directly; its value (98 Hz) is in fair agreement with the separation of 95 Hz obtained from the ^{31}P NMR spectrum. It seems clear, therefore, that the separations of 75−95 and 25 Hz in the doublet of doublets pattern of the PPh_2 resonances of **6**−**8** are due to ^4J and ^3J P−F couplings, respectively.

In free pentafluorophenylphosphines, such as $(C_6F_5)_3P$ and $C_6F_5PPh_2$, the largest P−F coupling constant of ca. 38 Hz (observed in the ^{19}F NMR spectrum) is due to $F^{2,6}$ (the *ortho*-fluorines), the *meta*- and *para*-couplings being close to zero.[29,53] Couplings similar to those of **6**−**8** are not observed in the ^{31}P NMR spectra of 2-$BrC_6F_4PPh_2$ or 2-$Me_3SnC_6F_4PPh_2$.[54] Possible reasons for these differences will be discussed below.

Dinuclear and Tetranuclear Complexes of Palladium(II). Heating of a mixture of **2** and $[PdCl_2(MeCN)_2]$ in toluene for 1 h gave an orange solution, from which a yellow solid of formula $[Pd_2Cl_2(C_6F_4PPh_2)_2]$ (**11**) was isolated in ca. 83% yield (Scheme 1). The ^{31}P NMR spectrum of **11** shows two broad singlets at δ −77.4 and −76.7 whose relative intensity varies in different preparations, indicating the presence of two species, both of which clearly contain four-membered chelate rings; the species responsible for the more shielded resonance is always the more abundant. Traces of a third compound having a ^{31}P NMR singlet at δ 28.7 are also observed (see below). The far-infrared spectrum of solid **11** shows two strong bands at 273 and 290 cm^{-1}, which are not present in the spectrum of **2** and can be assigned to the Pd−Cl stretching vibrations of a binuclear $Pd_2(\mu\text{-}Cl)_2$ unit.[55,56] The corresponding bands for the closely related, noncyclometalated complex $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(PPh_3)_2]$ appear at 270 and 290 cm^{-1}.[56] The data are consistent with the isomeric chloro-bridged structures *cis*-**11** and *trans*-**11** shown in Scheme 1; structure *trans*-**11** has been confirmed by X-ray crystallography.[57] A structurally similar chloride-bridged complex containing terminal cyclometalated $[2\text{-}MeC_6H_4C_6H_3P^tBu_2]^-$ ligands has also been reported recently.[58]

When a solution of **11** in CH_2Cl_2 was set aside at room temperature, a yellow precipitate of the same composition as

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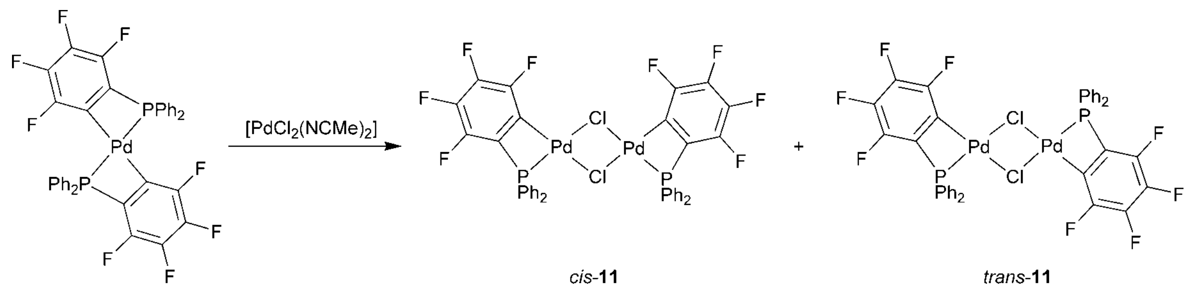
Scheme 1

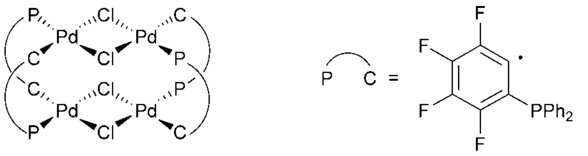


2

cis-**11**

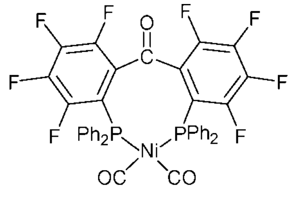
trans-**11**

11 slowly deposited. The ^{31}P NMR spectrum shows a singlet at δ 28.7, identical to that of the trace impurity observed during the preparation of **11**. This chemical shift is consistent with the presence of bridging $C_6F_4PPh_2$ groups resulting from opening of the four-membered chelate rings in **11**, and the far-infrared spectrum shows bands at 280 and 301 cm^{-1} assignable to bridging chloride ligands. The NMR and mass spectroscopic data indicate that this compound is a tetranuclear species, $[Pd_4(\mu\text{-}Cl)_4(\mu\text{-}2\text{-}C_6F_4PPh_2)_4]$ (**12**), which is isostructural with the known complexes $[Pd_4(\mu\text{-}X)_4(\mu\text{-}2\text{-}C_6H_4PPh_2)_4]$ (X = Cl, Br).[12,13] The bromo analogue of **12** has been obtained independently by oxidative addition of $2\text{-}BrC_6F_4PPh_2$ to $[Pd(dba)_2]$.[59]

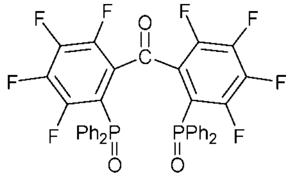


12

Reaction of Complex 3 with Carbon Monoxide. Complexes **1** and **2** are inert toward CO under ambient conditions, but the nickel(II) bis(chelate) complex **3** reacted with CO at room temperature over a period of 6 h to give an orange-red solution, from which an unstable yellow-orange solid (**13**) could be isolated. This shows a singlet in its ^{31}P NMR spectrum at δ 30.5 (C_6D_6) [δ 31.2 (CD_2Cl_2)] and two strong bands in the CO stretching region of the IR spectrum at 2021 and 1966 cm^{-1}, which are suggestive of a bis(tertiary phosphine)dicarbonylnickel(0) species.[60] There is also a strong band at 1684 cm^{-1}, which could be assigned to a bridging carbonyl, a ketonic carbonyl, or an aroyl group. Isolated samples of **13** were always contaminated with the oxidation product **14** (see below). When the solution was exposed to air, or when passage of CO was continued for 5 days, the color changed to yellow and a colorless solid (**14**) was isolated, the IR spectrum of which contained no C≡O stretching bands, but did show an intense band at 1203 cm^{-1}, a strong band at ca. 1700 cm^{-1}, and a broad absorption in the region of 3500 cm^{-1} assignable, respectively, to the P=O stretching frequency of a phosphine oxide, a ketonic carbonyl, and water. The water could not be removed, even after prolonged heating *in vacuo*. Compound **14** showed a singlet at δ 26.0 in its ^{31}P NMR spectrum and an intense peak at *m/z* 727 $[M + H]^+$ in its electrospray mass spectrum. The spectroscopic data are consistent with the formulation of **14** as the 2,2′-disubstituted benzophenone $\{2,2'\text{-}C_6F_4P(O)Ph_2\}_2CO$, and the elemental analysis corresponds to this composition together with ca. 1 equiv of water. The molecular structure of **14** determined by single-crystal X-ray diffraction analysis is shown in Figure 6, together with significant bond lengths and angles, which are unexceptional. The crystal selected contained ca. 0.6 mol/mol of water that is strongly hydrogen-bonded to the P=O groups following well-established behavior for tertiary phosphine oxides.[61]



13



14

Since **14** must arise from the initial insertion of CO into one of the Ni−C σ-bonds of **3**, we carried out the reaction of **3** in CD_2Cl_2 with ^{13}CO to see if aroyl intermediates could be detected. Concomitant with the growth of the singlet at δ 31.2 in the ^{31}P NMR spectrum, there appeared over a period of hours three singlets of approximately equal intensity in the ^{13}C NMR spectrum at δ 186.2, 195.4, and 197.8. The ^{31}P NMR singlet due to **3** disappeared completely only after ca. 48 h, having been replaced by the singlet at δ 31.2 and a weak peak at δ 24.5. No peaks were observed in the δ 220−280 region of the ^{13}C NMR spectrum attributable to an aroylnickel(II) intermediate, cf. δ(COAr) values of 253.0 (J_{PC} = 26.5 Hz) in *trans*-

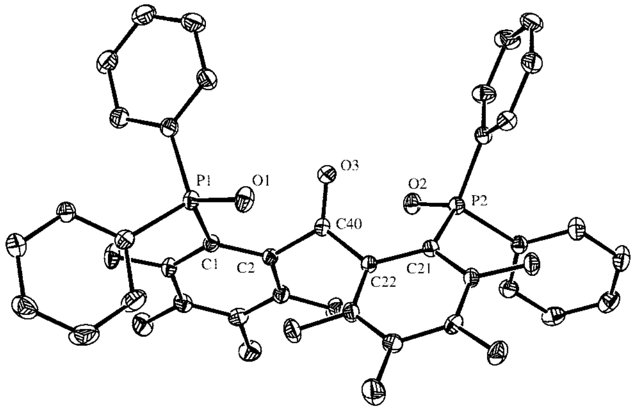


Figure 6. Molecular structure of $\{2,2'\text{-}C_6F_4P(O)Ph_2\}_2CO$ (**14**) with labeling of selected atoms. Ellipsoids show 30% probability levels. The H-bonded water molecule and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)−O(1) 1.4817(6), P(2)−O(2) 1.4793(16), C(40)−O(3) 1.205(2), O(1)−P(1)−C(1) 109.26(3), O(2)−P(2)−C(21) 111.16(9), C(22)−C(40)−O(3) 120.97(18), C(2)−C(40)−O(3) 119.92(18).

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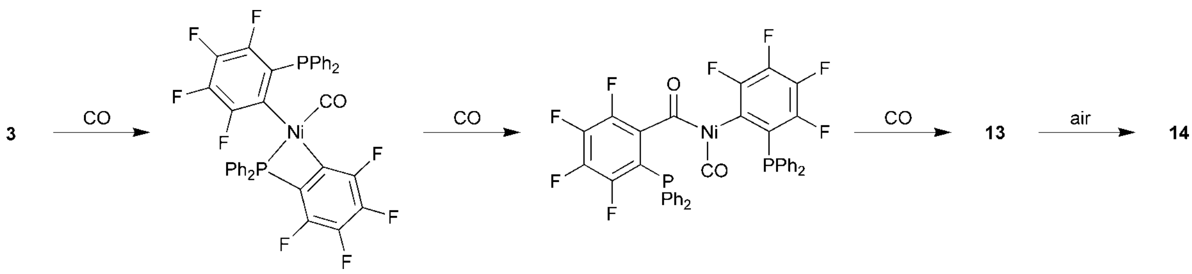
Scheme 2



[NiCl(COPh)(PMe$_3$)$_2$][62] and 256.6 (J_{PC} = 76, 18 Hz) in [Ni(κ^2-COC$_6$H$_4$CF$_2$CF$_2$)(dcpe)].[63]

We suggest tentatively that two of the three ^{13}C resonances in the δ 200 region are due to the terminal and ketonic carbonyl groups of the Ni(CO)$_2$ complex of bis-2,2′-(diphenylphosphino)octafluorobenzophenone, (2,2′-C$_6$F$_4$PPh$_2$)$_2$CO, acting as a bidentate P-donor; this species is the orange solid (**13**) that gives rise to the singlet at ca. δ 31 in the ^{31}P NMR spectrum. Its instability may be due to the presence of an eight-membered chelate ring. At this stage we cannot explain why there should be three ^{13}CO NMR resonances, and further work is required to account for this observation. It is clear, however, that the reductive elimination that generates the benzophenone must occur rapidly after CO insertion. A plausible reaction sequence is shown in Scheme 2. In the first step, CO is likely to displace one or both phosphorus atoms of **3**, thus allowing migration of the nickel−carbon σ-bond to the coordinated CO. Reductive elimination of the tetrafluoroaroyl and tetrafluoroaryl groups under CO then generates the Ni(CO)$_2$ complex **13**, which, in the presence of air, is oxidized to the phosphine oxide and released from the metal.

These conclusions are supported by results published after this paper had been submitted, which show that the metalacycles *cis*- or *trans*-[Ni(κ^2-2-C$_6$H$_4$OP^{i}Pr$_2$)$_2$] react with CO to give, as a result of insertion and subsequent reductive elimination, the dicarbonylnickel(0) complex of a chelate, benzophenone-based bis(phosphinite) ligand, {2,2′-C$_6$H$_4$OP^{i}Pr$_2$}$_2$CO.[64]

Although the ready insertion of CO into nickel(II)−alkyl and −aryl σ-bonds is a well-established reaction sequence,[64−68] the insertion step is usually unfavorable for electron-withdrawing groups such as C$_6$F$_5$;[69,70] indeed, facile decarbonylation of the presumed oxidative addition product of C$_6$F$_5$COCl and [Ni(C$_2$H$_4$)(PPh$_3$)$_2$] has been used to prepare [NiCl(C$_6$F$_5$)(PEt$_3$)$_2$].[71] It is of interest that the ability of [Ni(κ^2-2-C$_6$F$_4$PPh$_2$)$_2$] (**3**) to insert CO differs from the behavior of the complexes [Ni(κ^2-2-C$_6$Cl$_4$PR$_2$)$_2$] [R = Et (**5**), Ph], which reversibly add CO to give five-coordinate adducts in solution, but do not insert CO.[20]

Conclusions

Use of the carbanion [2-C$_6$F$_4$PPh$_2$]$^-$ in place of [2-C$_6$H$_4$PPh$_2$]$^-$ enables the isolation of the complete series of homoleptic bis(chelate) complexes of elements of the nickel triad. For all three elements, the stable isomer has the *trans*-configuration, whereas for platinum(II) with 2-C$_6$H$_4$PPh$_2$, the *trans*-isomer is only detectable as a transient intermediate on the way to the more stable *cis*-isomer. In this respect, the fluorinated carbanion seems to behave somewhat like a pseudohalide, behavior that is consistent with the lower *trans*-influence of C$_6$F$_5$ relative to C$_6$H$_5$, as assessed by J_{PtP} values in planar platinum(II) complexes.[72] The isolability of **2** and **3** and the different behavior of *cis*-[Pt(κ^2-2-C$_6$X$_4$PPh$_2$)$_2$] [X = F (**1**) and H (**4**)] on heating indicate the stabilizing effect of the fluorine substituents on the four-membered ring, although there is no evidence from comparisons of the Pt−C bond lengths that this effect is caused by a strengthening of the M−C σ-bond. Strain in the four-membered rings of **1**−**3** is indicated by the reactions of **1**−**3** with bidentate ligands and the ready carbonylation of the nickel complex **3**. However, the ring-opening of κ^2-2-C$_6$F$_4$PPh$_2$ is evidently slower than that of κ^2-2-C$_6$H$_4$PPh$_2$, since an intermediate analogous to [Pd$_2$(μ-Cl)$_2$(κ^2-2-C$_6$F$_4$PPh$_2$)$_2$] (**11**) has not been reported so far in the 2-C$_6$H$_4$PPh$_2$ series, despite the thermodynamically favored conversion of **11** to the tetranuclear, ring-opened complex **12** in solution.

Finally, we comment briefly on the unprecedentedly large values of $^4J_{PF}$ (75−95 Hz) to F^6, the fluorine atom *ortho* to the metal−carbon σ-bond, in the dppe complexes **6**−**8**. There are few systematic studies of vicinal and long-range P−F couplings.[73] Many long-range F−F couplings are believed to be "through space",[74] but this clearly cannot be the case for **6**−**8**, where the P−F coupling must be transmitted through the planar F−C−C−C−P unit. There is abundant evidence that ^{31}P−^{1}H and ^{31}P−^{13}C couplings through two or more bonds depend strongly on the dihedral angle (maximum at 0°, minimum at about 90°, according to the Karplus relationship) and, most importantly, on the geometric orientation relative to the lone pair on the phosphorus atom.[75,76] The same could well hold for long-range P−F couplings. The directions of the lone pairs at phosphorus atoms P(1) and P(2) in **6**, **8**, and **9** can be estimated from the molecular structures by inserting a phantom hydrogen atom at the expected position. The torsion angles

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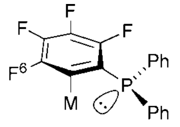

M = Ni (**6**), Pd (**7**), Pt (**8**)

Figure 7. Synperiplanar orientation of F^6 and lone pair of PPh_2 in complexes **6**−**8**.

C(6)−C(1)−P(1)−lone pair and C(24)−C(19)−P(2)−lone pair are, respectively, 7.9(2)°, 5.5(2)° (**6**), 8.9(2)°, 4.1(2)° (**8**), and 18.2(2)°, 20.3(2)° (**9**). In the dppe complexes **6** and **8**, therefore, the fluorine atom and the lone pair on the phosphorus atom of PPh_2 are much closer to a synperiplanar orientation than in the bipy complex **9**, as shown in Figure 7, possibly as a consequence of the steric bulk of dppe. This feature may account for the large $^4J_{PF}$ values in the dppe complexes.

Experimental Section

General Comments. All experiments involving organolithium reagents were performed under an atmosphere of dry argon with the use of standard Schlenk techniques. Diethyl ether, THF, and *n*-hexane were dried over sodium/benzophenone, toluene over sodium, and dichloromethane over calcium hydride. The complexes $[PtCl_2(SEt_2)_2]$,[77] $[PtI_2(COD)]$,[78] $[PdCl_2(SEt_2)_2]$,[79] $[PdBr_2(COD)]$,[80] and $[PdCl_2(NCMe)_2]$[81] were prepared by literature methods; all other reagents were commercially available and used as received. ^1H (300 MHz), ^{13}C (75 MHz) ^{19}F (282 MHz), and ^{31}P (121 MHz) NMR spectra were measured on a Bruker Avance 300 spectrometer at room temperature in $CDCl_3$, CD_2Cl_2, or C_6D_6. The ^{31}P NMR spectra **6**−**10** at 202 MHz were measured on an Varian Inova 500 spectrometer. Chemical shifts (δ) are given in ppm, internally referenced to residual solvent signals (^1H and ^{13}C), internal $CFCl_3$ (^{19}F), or external 85% H_3PO_4 (^{31}P). The ^{19}F−^{31}P HMQC experiment was recorded at a ^{19}F frequency of 282.3 MHz and a ^{31}P frequency of 121.5 MHz on a Varian Inova 300 spectrometer at a temperature of 297 K. The spectral widths were 29 000 and 9000 Hz in the F2 and F1 dimensions, respectively. The recycle delay was 1.5 s; 4K complex points were acquired in F2 and 128 increments of 128 scans in F1. The resolution in F1 was extended to 512 real points with linear prediction and the data zero-filled to 4K points. ^{19}F and ^{31}P NMR data for complexes **1**−**3** and **6**−**10** are given in Table 1; ^{31}P NMR data for complex **11** are given in Table 3.

Infrared spectra were obtained on a Perkin-Elmer Spectrum 2000 FT spectrometer as KBr or polythene discs; electrospray (ESI) and MALDI mass spectra were measured on HP 5970 MSD and Bruker Biflex II spectrometers, respectively. Elemental analyses were carried out by the Microanalytical Unit at the Research School of Chemistry, ANU.

X-ray Crystallography. Crystals of *cis*-**1** and the two forms of *trans*-**1** were selected from a batch containing an approximately 1:3 mixture of the two isomers obtained after recrystallization from CH_2Cl_2/hexane. Crystals of **2**, **3**, and **14** suitable for X-ray crystallography were obtained from CH_2Cl_2/hexane and crystals of **6**, **8**, and **9** from CH_2Cl_2/methanol. The crystals were coated in viscous oil and mounted on fine-drawn capillaries. Data were collected at 200 K on a Nonius-Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Crystal data and details of data collection are given in Table 4. Data were measured by use of COLLECT.[82] The intensities of reflections were extracted, and the data were reduced by use of the computer programs Denzo and Scalepack.[83] The crystal structures were solved by direct methods[84] and refined, either on F by use of the program CRYSTALS[85] in the case of **1**−**3**, on F^2 by use of the SHELX program[86] in the case of **6**, **8**, and **9**, or on F^2 by use of CRYSTALS[85] in the case of **14**. Neutral atom scattering factors,[87] the values of $\Delta f'$ and $\Delta f''$, and mass attenuation coefficients[88] were taken from standard compilations.

The water molecule in **14** was initially located in a difference electron density map. Refinement of the occupancy yielded a final value of 0.572(8); the hydrogen atoms of the water molecule were not located. The other hydrogen atoms were all observed in difference maps. They were put in at idealized positions and refined positionally.

Syntheses. $2\text{-}BrC_6F_4PPh_2$: (2-Bromo-3,4,5,6-tetrafluorophenyl)-diphenylphosphine was prepared by a literature method[22] in yields of 80−85%. Mp: 64−66 °C. ^1H NMR ($CDCl_3$): δ 7.3−7.5 (m). ^{13}C NMR ($CDCl_3$): δ 128.7 (d, J_{PC} 7.2 Hz), 129.2 (s), 132.9 (dd, $J = 1.5$, 21.2 Hz), 133.7 (dd, J 3.5, 11.4 Hz). Small multiplets at δ 112 and in the range 130−151 were also observed, presumably due to the C_6F_4Br carbons. ^{31}P NMR ($CDCl_3$): δ −1.58 (ddd, J_{PF} 4.4, 10.4, 20.5 Hz). ^{19}F NMR ($CDCl_3$): δ −121.8 (m), −126.6 (m), −150.2 (m), −154.1 (m). ESI-MS (*m/z*): 413 $[M + H]^+$. Anal. Calcd for $C_{18}H_{10}BrF_4P$: C 52.33; H 2.44; Br 19.37; P 7.50. Found: C 52.53; H 2.56; Br 19.21; P 7.13.

$[M(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)_2]$ [M = Pt (**1**), Pd (**2**)]: To a solution of $2\text{-}BrC_6F_4PPh_2$ (1.0 g, 2.4 mmol) in Et_2O (20 mL) cooled to −78 °C was added ^{n}BuLi (1.6 M, 1.5 mL, 2.4 mmol), and the mixture was stirred for 15 min. To the pale yellow solution was added solid $[MCl_2(SEt_2)_2]$ (1.1 mmol), and stirring was continued at −78 °C for 4 h, then at room temperature overnight. The pale yellow solid was filtered off, washed with a little Et_2O (caution: solid slightly soluble), and dissolved in CH_2Cl_2. The mixture was filtered to remove LiCl, MeOH was added to the filtrate, and the volume was reduced *in vacuo*. The white solid that precipitated was isolated by filtration, washed with MeOH, and dried. Yields were typically ca. 30% but could be increased to 39% and 66% by starting with $[PdBr_2(COD)]$ and $[PtI_2(COD)]$, respectively.

M = Pt (**1**): ^1H NMR ($CDCl_3$): δ 7.2−7.9 (m, 10H, aromatics). *cis/trans* ratio estimated from ^{31}P NMR spectrum ca. 1:3. ESI-MS (*m/z*): 862 $[M + H]^+$. Anal. Calcd for $C_{36}H_{20}F_8P_2Pt$: C 50.19; H 2.34; F 17.64. Found: C 49.73; H 2.60; F 17.31.

M = Pd (**2**): ^1H NMR ($CDCl_3$): δ 7.4−7.6 (m, 6H, aromatics), 7.8−7.9 (m, 4H, aromatics). ESI-MS (*m/z*): 772 $[M]^+$. Anal. Calcd for $C_{36}H_{20}F_8P_2Pd$: C 55.95; H 2.61; F 19.66. Found: C 56.21; H 2.86; F 19.32.

trans-$[Ni(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)_2]$ (**3**): A mixture of $2\text{-}BrC_6F_4PPh_2$ (1.0 g, 2.4 mmol) and anhydrous $NiCl_2$ (0.15 g, 1.15 mmol) in THF

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Table 4. Crystal and Refinement Data for *cis*-[Pt(κ^2-2-$C_6F_4PPh_2$)$_2$] (*cis*-1), *trans*-[M(κ^2-2-$C_6F_4PPh_2$)$_2$] [M = Pt (*trans*-1), Pd (2), Ni (3)], [M(κC-2-$C_6F_4PPh_2$)$_2$(L-L)] [M = Ni, L-L = dppe (6), bipy (9); M = Pt, L-L = bipy (8)], and {2,2′-$C_6F_4P(O)Ph_2$}$_2$CO (14)

	cis-**1**	*trans*-**1** (form A)	*trans*-**1** (form B)	**2**	**3**
formula	$C_{36}H_{20}F_8P_2Pt$	$C_{36}H_{20}F_8P_2Pt$	$C_{36}H_{20}F_8P_2Pt$	$C_{36}H_{20}F_8P_2Pd$	$C_{36}H_{20}F_8NiP_2$
fw	861.58	861.58	861.58	772.89	725.20
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/c$
cryst color, habit	pale yellow, plate	colorless, plate	colorless, needle	colorless, plate	yellow, plate
a (Å)	15.2827(5)	10.0072(2)	24.2624(4)	9.9970(2)	12.4710(3)
b (Å)	10.0943(3)	12.2049(2)	10.1948(2)	12.2158(2)	12.3859(3)
c (Å)	24.4836(8)	12.7603(2)	13.4835(2)	12.7955(2)	20.0281(4)
α (deg)					
β (deg)	103.3068(12)	104.9435(11)	113.5666(12)	105.0546(10)	97.9282(13)
γ (deg)					
V (Å^3)	3675.6(2)	1505.80(5)	3056.98(9)	1508.97(5)	3064.06(12)
Z	4	2	4	2	4
D_{calc} (g cm^{-3})	1.557	1.900	1.872	1.701	1.572
cryst dimens	0.43 × 0.23 × 0.20	0.32 × 0.24 × 0.13	0.34 × 0.08 × 0.03	0.28 × 0.26 × 0.14	0.23 × 0.14 × 0.05
μ (mm^{-1})	3.968	4.842	4.771	0.798	0.813
no. indep reflns (R_{int})	4189 (0.08)	3459 (0.03)	3505 (0.04)	3449 (0.04)	5458 (0.072)
no. obsd reflns	3509 [$I > 3\sigma(I)$]	2516 [$I > 3\sigma(I)$]	2198 [$I > 3\sigma(I)$]	2740 [$I > 3\sigma(I)$]	3608 [$I > 2\sigma(I)$]
no. params refined	213	214	215	214	424
R	0.0342[a]	0.0156[a]	0.0196[a]	0.0212[a]	0.0416[a]
R_w	0.0261[a]	0.0189[a]	0.0211[a]	0.0244[a]	0.0468[a]
GOF	1.1549	1.0454	1.1330	1.0688	1.0876
ρ_{max}/ρ_{min} (e Å^{-3})	1.40/−1.45	0.42/−0.90	0.67/−0.89	0.33/−0.53	0.94/−0.59

	6	**8**	**9**	**14**
formula	$C_{62}H_{44}F_8NiP_4$	$C_{62}H_{44}F_8P_4Pt$	$C_{46}H_{28}F_8N_2NiP_2$	$C_{37}H_{20}F_8O_3P_2 \cdot 0.572H_2O$
fw	1123.56	1259.94	881.35	736.77
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
cryst color, habit	yellow, plate	colorless, plate	black, prism	colorless, plate
a (Å)	12.6153(3)	12.6153(3)	14.8947(4)	9.6431(1)
b (Å)	12.7350(2)	12.7350(2)	16.9283(4)	12.5819(1)
c (Å)	17.2316(4)	17.2316(4)	15.8600(5)	26.2617(3)
α (deg)	81.8180(10)	81.8180(10)		
β (deg)	79.2260(10)	79.2260(10)	101.692(2)	98.1043(6)
γ (deg)	75.1250(10)	75.1250(10)		
V (Å^3)	2615.42(10)	2615.42(10)	3916.00(19)	3154.47(5)
Z	2	2	4	4
D_{calc} (g cm^{-3})	1.427	1.600	1.495	1.551
cryst dimens	0.32 × 0.11 × 0.05	0.30 × 0.11 × 0.08	0.10 × 0.08 × 0.08	0.24 × 0.18 × 0.04
μ (mm^{-1})	0.563	2.875	0.652	0.23
no. indep reflns (R_{int})	9235 (0.056)	11 972 (0.047)	6901 (0.0865)	7256 (0.049)
no. obsd reflns	9235 [$I > 2\sigma(I)$]	11 972 [$I > 2\sigma(I)$]	6901 [$I > 2\sigma(I)$]	4515 [$I > 2\sigma(I)$]
no. params refined	677	677	533	521
R	0.0366[b]	0.0270[b]	0.0402[b]	0.032[b]
R_w	0.0952[b]	0.0541[b]	0.0860[b]	0.105[b]
GOF	1.037	1.022	1.030	0.99
ρ_{max}/ρ_{min} (e Å^{-3})	0.615/−0.435	0.563/−0.836	0.363/−0.327	0.44/−0.45

[a] Refined on F. [b] Refined on F^2.

(20 mL) was refluxed for 24 h, then zinc dust (0.11 g, 1.6 mmol) was added and heating was continued for a further 48 h. The solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2. Filtration through Celite gave an orange solution, to which MeOH was added. The volume of the solution was reduced *in vacuo*, and the yellow solid that precipitated was isolated, washed with MeOH, and dried (0.25 g, 30%). ^1H NMR ($CDCl_3$): δ 7.4−7.6 (m, 6H, aromatics), 7.8−7.9 (m, 4H, aromatics). ESI-MS (*m*/*z*): 725 [M + H]$^+$. Anal. Calcd for $C_{36}H_{20}F_8P_2Ni$: C 59.63; H 2.78; F 20.96. Found: C 59.29; H 2.97; F 21.05.

cis-[M(κC-C_6F_4-2-PPh_2)$_2$(dppe)] [M = Ni (**6**), Pd (**7**), Pt (**8**)]: To a solution of the appropriate bis(chelate) (0.07 mmol) in CH_2Cl_2 (3 mL) was added solid dppe (28 mg, 0.07 mmol), and the mixture was stirred for 10 min. Hexane was added, the volume was reduced *in vacuo*, and the precipitate was isolated by filtration. The solid was washed with hexane and dried *in vacuo*.

M = Ni (**6**): yellow solid (67 mg, 85%). ^1H NMR (C_6D_6): δ 1.77 (m, 4H, CH_2), 6.7−7.3 (m, 32H, aromatics), 7.26 (m, 4H, aromatics), 8.47 (m, 4H, aromatics). ESI-MS (*m*/*z*): 1122 [M]$^+$. Anal. Calcd for $C_{62}H_{44}F_8P_4Ni$: C 66.28; H 3.95; F 13.53. Found: C 66.28; H 4.21; F 13.10.

M = Pd (**7**): colorless solid (60 mg, 73%). ^1H NMR (C_6D_6): δ 1.80 (m, 4H, CH_2), 6.7−7.1 (m, 32H, aromatics), 7.28 (t, 4H, *J* 7.0 Hz, aromatics), 8.22 (t, 4H, *J* 8.4 Hz, aromatics). ESI-MS (*m*/*z*): 1170 [M]$^+$. Anal. Calcd for $C_{62}H_{44}F_8P_4Pd$: C 63.58; H 3.79; F 12.98. Found: C 63.45; H 4.07; F 12.60.

M = Pt (**8**): colorless solid (69 mg, 78%). ^1H NMR (C_6D_6): δ 1.74 (m, 4H, CH_2), 6.8−7.1 (m, 32H, aromatics), 7.28 (t, 4H, *J* 7.0 Hz, aromatics), 8.26 (dd, 4H, *J* 8.1, 9.9 Hz, aromatics). ESI-MS (*m*/*z*): 1259 [M]$^+$. Anal. Calcd for $C_{62}H_{44}F_8P_4Pt$: C 59.10; H 3.52; F 12.06. Found: C 58.23; H 3.83; F 11.88.

cis-[Ni(κC-C_6F_4-2-PPh_2)$_2$(L-L)] [L-L = bipy (**9**), phen (**10**)]: To a solution of complex **3** (93 mg, 0.13 mmol) in CH_2Cl_2 (10 mL) was added solid L-L (0.13 mmol). The yellow solution immediately turned dark and was stirred for 10 min. Hexane was added, and the solution was evaporated under reduced pressure. The precipitated solid was isolated by filtration, washed with hexane, and dried *in vacuo*.

L-L = 2,2′-bipyridine (**9**): brown solid (104 mg, 89%). ^{1}H NMR (CD_2Cl_2): δ 6.66 (m, 2H, bipy), 6.9−7.3 (m, 22H, aromatics + bipy), 7.63 (m, 2H, bipy), 7.77 (m, 2H, bipy). ESI-MS (*m/z*): 880 $[M]^+$. Anal. Calcd for $C_{46}H_{28}F_8N_2P_2Ni$: C 62.69; H 3.20; N 3.18; F 17.24. Found: C 62.48; H 3.37; N 3.10; F 16.99.

L-L = 1,10-phenanthroline (**10**): black solid (112 mg, 96%). ^{1}H NMR (CD_2Cl_2): δ 6.71 (t, 4H, *J* 7.2 Hz, aromatics), 6.84 (t, 4H, *J* 7.2 Hz, aromatics), 6.92 (dd, 2H, *J* 5.1, 8.2 Hz, phen), 7.08 (t, 2H, *J* 7.0 Hz, aromatics), 7.19 (m, 10H, aromatics), 7.37 (dd, 2H, *J* 1.1, 5.1 Hz, phen), 7.88 (s, 2H, phen), 8.09 (dd, 2H, *J* 1.0, 8.4 Hz, phen). ESI-MS (*m/z*): 904 $[M]^+$. Anal. Calcd for $C_{48}H_{28}F_8N_2P_2Ni$: C 63.68; H 3.12; N 3.09; F 16.79. Found: C 63.60; H 3.22; N 3.01; F 16.86.

$[Pd_2(\mu\text{-}Cl)_2(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)_2]$ (**11**): A mixture of complex **2** (355 mg, 0.46 mmol) and $[PdCl_2(MeCN)_2]$ (119 mg, 0.46 mmol) suspended in dry toluene (20 mL) was heated to 65 °C for 1 h, during which time the color changed from yellow to orange-red. The solvent was removed *in vacuo*, and the residue was recrystallized from CH_2Cl_2/hexane to give **11** as a yellow solid (360 mg, 83%). ^{1}H NMR (CD_2Cl_2): δ 7.2−8.1 (m, 20H, aromatics). ^{31}P NMR (CD_2Cl_2): δ −77.4 (s), −76.7 (s) (**11**), 28.7 (s) (trace of **12**). ^{19}F (CD_2Cl_2): δ −129.7 (m), −130.8 (m), −134.1 (m), −134.3 (m), −146.7 (m), −147.0 (m), −157.4 (m), −157.5 (m). Far-IR (polythene, cm^{-1}): 273, 290 (Pd−Cl str). MALDI-MS (*m/z*): 915 $[M - Cl]^+$. Anal. Calcd for $C_{36}H_{20}Cl_2F_8P_2Pd_2$: C 45.51; H 2.12; Cl 7.46; F 16.00. Found: C 45.90; H 2.42; Cl 7.29; F 15.41.

$[Pd_4(\mu\text{-}Cl)_4(\mu\text{-}2\text{-}C_6F_4PPh_2)_4]$ (**12**): A solution of complex **11** (120 mg, 0.13 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 1 week, during which time a yellow solid precipitated. The volume was reduced to half *in vacuo*, and acetone was added. The suspension was filtered, and the solid was washed with acetone and Et_2O, and dried *in vacuo* (49 mg, 41%). ^{1}H NMR (CD_2Cl_2): δ 7.2−7.6 (m, 40H, aromatics). ^{31}P NMR (CD_2Cl_2): δ 28.7 (s). ^{19}F NMR (CD_2Cl_2): δ −103.6 (m), −117.1 (m), −146.6 (m), −158.8 (m). Far-IR (polythene, cm^{-1}): 280, 301 (Pd−Cl str). MALDI-MS (*m/z*): 1865 $[M - Cl]^+$. Anal. Calcd for $C_{72}H_{40}Cl_4F_{16}P_4Pd_4$: C 45.51; H 2.12; Cl 7.46; F 16.00. Found: C 45.19; H 2.22; Cl 7.46; F 15.68.

$\{2,2'\text{-}C_6F_4P(O)Ph_2\}_2CO$ (**14**): A solution of **3** (115 mg, 0.16 mmol) in CH_2Cl_2 (20 mL) was stirred in an atmosphere of CO for 5 days, during which time the color changed from yellow to orange (immediately) to red (several hours) and finally back to yellow (several days). The solvent was evaporated to small volume *in vacuo*, and the residue was transferred to a silica gel column. The product was eluted with ethyl acetate. The volume of the eluate was reduced *in vacuo*, and hexane was added. Evaporation gave a colorless solid, which was isolated by filtration, washed with hexane, and dried *in vacuo*. The yield of $\{2,2'\text{-}C_6F_4P(O)Ph_2\}_2CO$ (**14**), mp ca. 240 °C (dec), was 85 mg (74%). ^{1}H NMR ($CDCl_3$): δ 1.67 (br s, 2H, H_2O), 7.4−7.8 (m, 20H, aromatics). ^{13}C NMR ($CDCl_3$): δ 128.5 (dd, *J* 7.6, 13.1 Hz), 130.2 (d, *J* 112.7 Hz), 131.4 (dt, *J* 2.3, 11.5, 11.5 Hz), 132.3 (dd, *J* 3.0, 8.6 Hz), 180.5 (m). Small multiplets at δ 119 and in the range 140−150 were also observed, presumably due to the C_6F_4 carbons. ^{31}P NMR ($CDCl_3$): δ 26.0 (s). ^{19}F NMR ($CDCl_3$): δ −120.9 (m), −134.7 (m), −146.7 (m), −148.9 (m). IR (KBr, cm^{-1}): 3468 (O−H str), 3055 (C−H str), 1707 (C═O str), 1203 (P═O str). ESI-MS (*m/z*): 727 $[M + H]^+$. Anal. Calcd for $C_{37}H_{20}F_8O_3P_2\cdot H_2O$: C 59.77; H 2.96; F 20.33; P 8.33. Found (different samples): C 58.82, 59.25; H 2.88, 3.09; F 20.11, 19.98; P 7.84, 7.86.

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Note Added after ASAP Publication. In the version of this paper published on the Web on Sept. 9, 2008, refs 77−88 were misnumbered. In addition, the data for compounds **2** and **3** in Table 4 were merged together. These errors have been corrected in the version of the paper that now appears.

Supporting Information Available: X-ray crystallographic data in CIF format for complexes **1**−**3**, **6**, **8**, **9**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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