Synthesis and Nucleophilic Behavior of *cis*-$[M(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ (M = Pd, Pt): C-Alkylation, Metalation, and Halogenation of Coordinated Bis(diphenylphosphino)methane. X-ray Crystal Structure of $[Pt(C_6F_5)_2(Ph_2PCHIPPh_2)]\cdot C_5H_{12}$

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The reaction of the neutral complexes *cis*-$[M(C_6F_5)_2(Ph_2PCH_2PPh_2)]$ [M = Pd (**1a**), Pt (**1b**)] with LDA (lithium diisopropylamide) or Li^tBu (*tert*-butyllithium) in THF readily affords the anionic derivatives $[M(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ by deprotonation of the coordinated bis(diphenylphosphino)methane (dppm). The reactivity of the carbanionic center thus generated toward a variety of substrates has been studied. The reaction with alkyl halides such as MeI or EtI gives the neutral, C-alkylated complexes *cis*-$[M(C_6F_5)_2(Ph_2PCHRPPh_2)]$ [M = Pd, R = Me (**2a**), Et (**4a**); M = Pt, R = Me (**2b**), Et (**4b**)], and the reaction with $ClAuPPh_3$ or $O_3ClOAgPPh_3$ gives the heterobimetallic species *cis*-$M(C_6F_5)_2[Ph_2PCH(M'PPh_3)PPh_2]$ [M = Pd, M′ = Au (**5a**), Ag (**6a**); M = Pt, M′ = Au (**5b**), Ag (**6b**)], in which the $[Ph_2PCHPPh_2]^-$ ligand acts as a bridging, tridentate-*P*,*P′*,*C* ligand. The reactions with halogens (Cl_2, Br_2, I_2) or pentafluorophenyl halides (BrC_6F_5, IC_6F_5) produce the heterolytic cleavage of the X−X or X−C bond, giving the halogenated derivatives *cis*-$[M(C_6F_5)_2(Ph_2PCHXPPh_2)]$ [M = Pd, X = I (**9a**); M = Pt, X = Cl (**7b**), Br (**8b**), I (**9b**)]. The reaction of $[Pt(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ with C_6F_5CN occurs with C−F bond cleavage, and the para-substituted product $M(C_6F_5)_2[Ph_2PCH(C_6F_4CN\text{-}4)PPh_2]$ (**10b**) is obtained. The X-ray crystal structure of **9b**$\cdot C_5H_{12}$ is reported.

Introduction

Bis(diphenylphosphino)methane ($Ph_2PCH_2PPh_2$ or dppm) is, among the diphosphine compounds, one of the most commonly employed ligands in inorganic and organometallic chemistry.[1] Its wide range of applicability extends from the synthesis of homo- and heteropolynuclear clusters[1] to homogeneous catalysis.[2] The related compound bis(diphenylphosphino)methanide $[Ph_2PCHPPh_2]^-$ (obtained from deprotonation of dppm) has also been widely used in the synthesis of polynuclear complexes.[3]

One of the most interesting applications of the complexes containing the methanide form arises from their use as intermediates in the synthesis of complexes with functionalized dppm, since it has been shown[4] that the treatment of the free ligand salts $[Li(Ph_2PCHPPh_2)]$ with electrophiles generally gives mixtures of products resulting from attack on carbon and phosphorus atoms. For instance, complexes with C-alkylated dppm have been reported,[5] and only very recently have halogenation reactions of the coordinated $[Ph_2PCHPPh_2]^-$ been described[6] in which, in almost all cases, carbonyl derivatives of transition metals with low oxidation numbers have been used. Despite this, the use of bis(diphenylphosphino)methanide complexes of M^{II} (M = Pd, Pt) in alkylation reactions has barely been examined,[5c,f] and, as far as we know, there are no examples of halogenation and/or metalation reactions.

We report here the synthesis of the anionic derivatives $[M(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ (M = Pd, Pt) and their reactivity as nucleophiles in alkylation, halogenation, and metalation reactions, all of which are “site-selective” to the bridgehead carbon atom. We also discuss the scope of their application to the synthesis of functionalized dppm.

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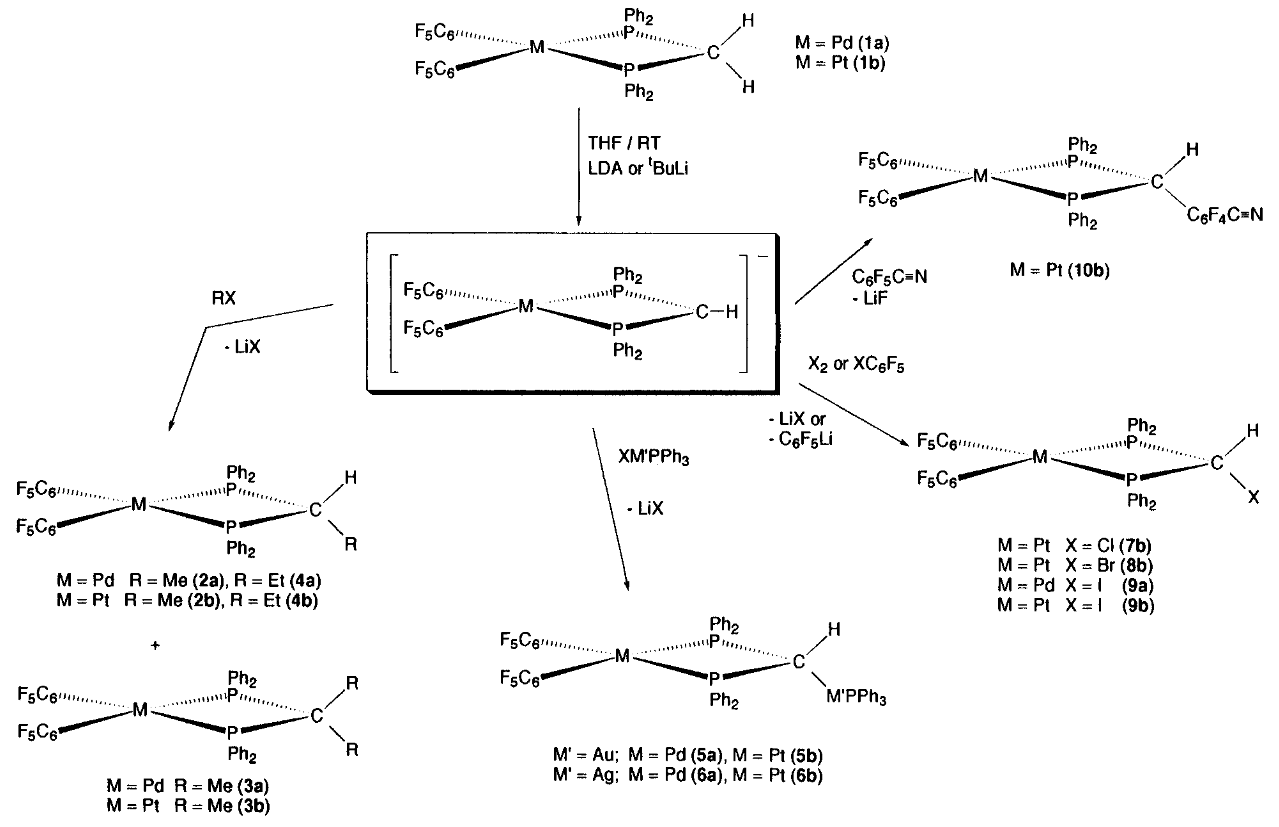
Scheme 1. Schematic Representation of the Reactions Performed for the Synthesis of Complexes 2a–10b



Results and Discussion

Synthesis of $[M(C_6F_5)_2(Ph_2PCHPPh_2)]^-$. We have recently shown that a convenient route for the synthesis of bis(diphenylphosphino)methanide derivatives of M^{II} (M = Pd, Pt) is the treatment of acac-*O,O′* complexes with a stoichiometric amount of dppm.[7] However, the reaction of $(NBu_4)[M(C_6F_5)_2(acac)]$ with dppm (1:1 molar ratio) does not afford the expected $(NBu_4)[M(C_6F_5)_2(Ph_2PCHPPh_2)]$ methanide complexes. Instead, the neutral species $M(C_6F_5)_2(dppm)$ are obtained. Furthermore, treatment of $M(C_6F_5)_2(dppm)$ with ^nBuLi in C_6H_6 or THF also fails to yield the corresponding methanide derivatives; the starting compounds are recovered unaltered.

We had more success using other strong bases such as LDA (lithium diisopropylamide, LiN^iPr_2) or ^tBuLi (*tert*-butyllithium). In fact, the reaction between $M(C_6F_5)_2(dppm)$ [M = Pd (**1a**), Pt (**1b**)] and LDA or ^{t}BuLi (molar ratio 1:1.2) in THF at room temperature gives deep yellow solutions of the carbanionic complexes $[M(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ (see Scheme 1). These solutions are quite air- and moisture-sensitive, and upon exposure to air, the yellow color disappears in a few seconds, indicating the protonation of the carbanionic center. This behavior contrasts markedly with the relatively high air and moisture stability of the related neutral complexes $[M(C_6F_5)(Ph_2PCHPPh_2)(PR_3)]$.[7] Because of that, freshly prepared solutions of $[M(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ are used in the reactions to be described.

Alkylation Reactions. The reaction between $[M(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ (M = Pd, Pt) and an excess of MeI (molar ratio ranging from 1:5 to 1:10, see the Experimental Section) affords the C-monoalkylated derivatives $[M(C_6F_5)_2(Ph_2PCHMePPh_2)]$ [M = Pd (**2a**), Pt (**2b**)], together with small amounts (less than 10%) of the dialkylated derivatives $[M(C_6F_5)_2(Ph_2PCMe_2PPh_2)]$ [M = Pd (**3a**), Pt (**3b**)] (see Scheme 1), through a typical aliphatic nucleophilic substitution process. Complexes **2a** and **2b** can be isolated in analytically pure form by recrystallization of the mixtures from CH_2Cl_2/*n*-hexane. The $^{31}P\{^1H\}$ NMR spectra of both complexes (see Table 1) show a single resonance, with ^{195}Pt satellites for **2b**, slightly broadened due to the presence of the *trans*-C_6F_5 groups. This resonance has undergone a downfield shift with respect to the starting dppm compounds **1a** or **1b** of the same magnitude as that observed for the complexes $M(CO)_4$(dppm-Me) (M = Cr, Mo, W)[5c] or PtX_2(dppm-Me).[5c] The ^1H NMR spectra show a triplet of quartets at about 4.7–4.9 ppm, attributed to the P_2CH proton, and a triplet of doublets at about 1.0–1.2 ppm, attributed to the P_2CMe unit. These observations show that the methylation process has been produced selectively at the central (*C*H) carbon atom and not at the phosphorus atom. The simultaneous observation of the coupling constants $^1J_{Pt-P}$, $^2J_{P-H}$, $^3J_{P-H}$, and $^3J_{H-H}$ indicates that the ring MP_2CHMe behaves as a rigid body in solution and that there are no proton interchange processes, which could give an inversion in the configuration at the central carbon atom. This point is important in the discussion of the ^{19}F NMR spectra (see the following).

The dialkylated complexes $[M(C_6F_5)_2(Ph_2PCMe_2PPh_2)]$ [M = Pd (**3a**), Pt (**3b**)], which were obtained as impurities in the synthesis of **2a** and **2b**, were not isolated in pure form, but they were characterized spectroscopically by ^1H and $^{31}P\{^1H\}$ NMR (see Table 1).

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Table 1. ^{1}H and ^{31}P{^{1}H} NMR Data [δ (ppm), J (Hz)] for Complexes 2a−10b

compound	δ(C−H)	$^2J_{P-H}$	others	δ(M−P)	δ(M′−P)	$^1J_{Pt-P}$	$^3J_{P-P}$
Pd(C_6F_5)$_2$(dppm-Me) (**2a**)	4.89 (tq)	14.0	1.22 (Me, td) $^3J_{P-H} = 14$; $^3J_{H-H} = 7$	−16.60			
Pt(C_6F_5)$_2$(dppm-Me) (**2b**)	4.73 (tq)	12.5	1.06 (Me, td) $^3J_{P-H} = 15$; $^3J_{H-H} = 7.4$	−27.89		1991	
Pd(C_6F_5)$_2$(dppm-Me$_2$) (**3a**)			1.72 (Me, t) $^3J_{P-H} = 15$	1.25			
Pt(C_6F_5)$_2$(dppm-Me$_2$) (**3b**)			1.46 (Me, t) $^3J_{P-H} = 15.3$	−10.55		2085	
Pd(C_6F_5)$_2$(dppm-Et) (**4a**)	4.56 (tt)	12 $^3J_{H-CH_2} = 6.9$	1.56 (CH$_2$, m); 0.93 (Me, t) $^3J_{CH_2-CH_3} = 7.3$	−14.73			
Pt(C_6F_5)$_2$(dppm-Et) (**4b**)	4.57 (m)	12 $^3J_{H-CH_2} = 7.2$	1.42 (CH$_2$, m); 0.92 (Me, t) $^3J_{CH_2-CH_3} = 7.3$	−26.42		1991	
Pd(C_6F_5)$_2$(dppm-AuPPh$_3$) (**5a**)	4.35 (q)	8.0		−24.91	40.60		9
Pt(C_6F_5)$_2$(dppm-AuPPh$_3$) (**5b**)	5.33 (q)	8.6	$^3J_{CH-Pt} = 104$	−35.39	40.16	1991	12
Pd(C_6F_5)$_2$(dppm-AgPPh$_3$) (**6a**)	4.09 (br)	7.9		−27.69	15.2 $^1J_{P-^{109}Ag} = 560.9$; $^1J_{P-^{107}Ag} = 487.7$		
Pt(C_6F_5)$_2$(dppm-AgPPh$_3$)[a] (**6b**)	5.29 (t, br)	8.0		−39.13	14.99 $^1J_{P-^{109}Ag} = 573.5$; $^1J_{P-^{107}Ag} = 496.9$	1963	6.5
Pt(C_6F_5)$_2$(dppm-Cl) (**7b**)	5.92 (t)	10.1		−6.89		1970	
Pt(C_6F_5)$_2$(dppm-Br) (**8b**)	6.06 (t)	10		−10.87		1966	
Pd(C_6F_5)$_2$(dppm-I) (**9a**)	6.08 (t)	10.6		−6.35			
Pt(C_6F_5)$_2$(dppm-I) (**9b**)	6.01 (t)	10.7		−18.53		1916	
Pt(C_6F_5)$_2$(dppm-C_6F_4CN) (**10b**)	6.53 (t)	12		−20.44		2040	

[a] −80 °C; t, triplet; tt, triplet of triplets; tq, triplet of quartets; td, triplet of doublets; m, multiplet; q, quartet; br, broad.

The ^{31}P{^{1}H} NMR spectra show a single resonance shifted downfield with respect to **2a** or **2b** by nearly the same displacement as that found for the complexes M(CO)$_4$(dppm-Me$_2$) (M = Cr, Mo, W)[5c] or PtX$_2$(dppm-Me$_2$).[5c] The ^{1}H NMR spectra show a triplet resonance (about 1.5 ppm) attributed to the CMe$_2$ unit.

Despite the clear reactivity observed between [M(C_6F_5)$_2$($Ph_2PCHPPh_2$)]$^-$ and MeI, the alkylation process with EtI is not so straightforward. In fact, when these reactions are carried out under the same conditions as those described for **2a** or **2b** (see Experimental Section), a mixture of the C-ethylated complexes [M(C_6F_5)$_2$($Ph_2PCHEtPPh_2$)] [M = Pd (**4a**), Pt (**4b**)] and the corresponding starting compounds **1a** or **1b** (molar ratio around 1.3:1) is obtained. An excess of the deprotonating agent and/or longer reaction times (up to 24 h) do not improve the percentage of conversion. We have attempted the separation of the two products by repeated recrystallizations, but in all cases we obtain, both in the crystallized fraction as well as in the mother liquor, a mixture of the same (or nearly the same) composition, probably due to the similar solubilities of these complexes. However, the complete spectroscopic characterization of **4a** and **4b** has been possible. The ^{31}P{^{1}H} NMR spectra show a single resonance in the same region as that found for **2a** or **2b** (see Table 1). The ^{1}H NMR spectra show the expected resonances for the MP$_2$C(H)CH$_2$CH$_3$ unit: a complex multiplet of relative intensity 1 around 4.6 ppm (CH), another multiplet of relative intensity 2 centered about 1.5 ppm (CH$_2$), and a triplet (intensity 3) at 0.9 ppm (CH$_3$).

The results obtained contrast with the easy C-ethylation[5c] of [PtI$_2$($Ph_2PCHPPh_2$)]$^-$, but could be explained by taking into account the withdrawing ability of the pentafluorophenyl ligands. A lower electronic density at the metal center would give a less nucleophilic carbanionic group, as in our case. The same result (partial conversion) is observed when the anions [M(C_6F_5)$_2$($Ph_2PCHPPh_2$)]$^-$ are allowed to react with PhCH$_2$Br, although in this case the conversion is even worse (ca. 20%). Finally, no reaction is observed between [M(C_6F_5)$_2$($Ph_2PCHPPh_2$)]$^-$ and ^{n}PrI or ^{i}PrI. The observed lack of reactivity could be due to the contribution of two concomitant factors: (i) the already discussed withdrawing nature of the C_6F_5 ligands and (ii) the known decreasing alkylating power in the series MeI > EtI, PhCH$_2$Br > ^{n}PrI, ^{i}PrI for the aliphatic nucleophilic substitution.

Reactions with Electrophilic Metal Substrates. The anionic complexes [M(C_6F_5)$_2$($Ph_2PCHPPh_2$)]$^-$ (M = Pd, Pt) react with ClAuPPh$_3$ or O$_3$ClOAgPPh$_3$ (molar ratio 1:1; see Scheme 1) to give the heterobimetallic derivatives M(C_6F_5)$_2$[Ph$_2$PCH(M′PPh$_3$)PPh$_2$] [M = Pd, M′ = Au (**5a**), Ag (**6a**); M = Pt, M′ = Au (**5b**), Ag (**6b**)] in moderate to good yields. Attempts to obtain the silver derivatives by reaction of [M(C_6F_5)$_2$($Ph_2PCHPPh_2$)]$^-$ with ClAgPPh$_3$ were not successful, yielding unaltered ClAgPPh$_3$ at the end of the reaction together with [M(C_6F_5)$_2$($Ph_2PCH_2PPh_2$)], with the protonation having occurred during the workup.

The spectroscopic data for these complexes show that the incorporation of the [M′PPh$_3$]$^+$ fragment has occurred at the methanide center. Thus, the ^{31}P{^{1}H} NMR spectra of the gold derivatives **5a** and **5b** (see Table 1) show the presence of two resonances: a broad singlet at high field (−24.9 ppm for **5a** and −35.4 ppm for **5b** with ^{195}Pt satellites, both slightly broadened by the presence of *trans*-C_6F_5 groups) attributed to the phosphorus of the MPCP ring and another resonance at low field (around 40 ppm) with triplet structure ($^3J_{P-P}$ coupling with the phosphorus of the MPCP ring) and attributed to the PPh$_3$ ligand linked to the gold atom. The resonance of the methine proton appears in the ^{1}H NMR spectra as a false quartet ($^2J_{P-H} \cong {}^3J_{P-H}$) and also shows ^{195}Pt satellites for **5b**. The ^{31}P{^{1}H} NMR spectrum of **6a** also shows a singlet resonance at high field (MPCP ring) and a doublet of doublets (coupling with ^{109}Ag and ^{107}Ag) at low field due to the PPh$_3$ ligand bonded to the silver center. A similar pattern of resonances is observed for complex **6b** although in this case the spectrum has to be measured at low temperatures to observe the complete splitting of the PPh$_3$ signal (doublet of doublets of triplets: coupling with ^{109}Ag and ^{107}Ag and with the P nucleus of the MPCP ring),

Table 2. ^{19}F NMR Data [δ (ppm), J (Hz)] for Complexes 2a−10b

compound	$\delta(F_o)$	$\delta(F_p)$	$\delta(F_m)$	$\delta(F_o)$	$\delta(F_p)$	$\delta(F_m)$ (−90 °C/CD_2Cl_2)
$Pd(C_6F_5)_2$(dppm-Me) (**2a**)	−115.07	−162.65	−164.72	−114.00 −115.77	−161.28	−163.60
$Pt(C_6F_5)_2$(dppm-Me) (**2b**)	−116.94 $^3J_{Pt-F_o} = 322$	−162.43	−164.38	−116.04 −117.84	−161.34 $^3J_{Pt-F_o} = 318$	−163.42 $^3J_{Pt-F_o'} = 336$
$Pd(C_6F_5)_2$(dppm-Et) (**4a**)	−115.06	−161.86	−163.98	−113.58 −115.31	−160.85	−163.07
$Pt(C_6F_5)_2$(dppm-Et) (**4b**)	−117.06 $^3J_{Pt-F_o} = 338$	−162.55	−164.37	−116.25 −117.99	−161.40 $^3J_{Pt-F_o} = 310$	−163.37 $^3J_{Pt-F_o'} = 318$
$Pd(C_6F_5)_2$(dppm-AuPPh$_3$) (**5a**)	−113.33	−162.79	−164.42	−110.73 −112.48	−161.47	−163.10
$Pt(C_6F_5)_2$(dppm-AuPPh$_3$) (**5b**)	−117.14 $^3J_{Pt-F_o} = 340$	−162.98	−164.19	−116.53 −117.12	−162.48 $^3J_{Pt-F_o} = 347$	−163.80 $^3J_{Pt-F_o'} = 333$
$Pd(C_6F_5)_2$(dppm-AgPPh$_3$) (**6a**)	−115.00	−161.77	−163.86	−112.45 −113.78	−160.75	−162.89
$Pt(C_6F_5)_2$(dppm-AgPPh$_3$) (**6b**)	−114.32 $^3J_{Pt-F_o} = 324$	−158.80	−160.92	−114.41 −115.03	−162.66 $^3J_{Pt-F_o} = {}^3J_{Pt-F_o'} = 356$	−163.90
$Pt(C_6F_5)_2$(dppm-Cl) (**7b**)	−117.50 $^3J_{Pt-F_o} = 370$	−161.51	−163.99			
$Pt(C_6F_5)_2$(dppm-Br) (**8b**)	−116.95 $^3J_{Pt-F_o} = 332$	−161.63	−163.94	−116.98 −118.75	−161.43 $^3J_{Pt-F_o} = 339$	−163.94 $^3J_{Pt-F_o'} = 325$
$Pd(C_6F_5)_2$(dppm-I) (**9a**)	−115.13	−160.91	−163.45	−114.88 −115.20	−160.22	−162.95
$Pt(C_6F_5)_2$(dppm-I) (**9b**)	−117.80 $^3J_{Pt-F_o} = 324$	−161.65	−164.08	−116.65 −118.18	−160.93 $^3J_{Pt-F_o} = 336$	−163.36 $^3J_{Pt-F_o'} = 336$
$Pt(C_6F_5)_2$(dppm-C_6F_4CN) (**10b**)	−117.68 $^3J_{Pt-F_o} = 327$	−161.45	−163.93	−114.99 −116.50	−160.94 $^3J_{Pt-F_o} = 338$	−163.42 $^3J_{Pt-F_o'}$ (nr)
	C_6F_4CN: −130.20 (br), −130.92 (d)				−129.87, −131.67, −131.97, −135.36	

[a] br, broad; d, doublet; nr, not resolved.

which at room temperature appears very broadened (see the following for the ^{19}F NMR discussion).

For complexes **5a**, **5b**, and **6a**, the NMR data are in keeping with the rigid behavior of the $MP_2CH(M'PPh_3)$ ring in solution, while for **6b** equilibrium dissociative processes must be present at room temperature.[8] Moreover, they confirm that the $[Ph_2PCHPPh_2]^-$ group is acting as a tridentate, six-electron donor ligand. As far as we know, these are the first examples of this coordination mode in palladium and platinum chemistry, obtained through the deliberate use of the chelating $[Ph_2PCHPPh_2]^-$ group as a C donor ligand to another metal center.

Halogenation Reactions. The nucleophilic character at the central carbon atom in the methanides $[M(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ can also promote the heterolytic cleavage of the halogen−halogen bond in dihalogen molecules such as Cl_2, Br_2, or I_2 and even that of the halogen−carbon bond in species such as BrC_6F_5 or IC_6F_5 (see Scheme 1 and the Experimental Section). Thus, $[Pt(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ reacts in THF with Cl_2 (1:1 molar ratio) to give $[Pt(C_6F_5)_2(Ph_2PCHClPPh_2)]$ (**7b**), but the conversion obtained is low (10%). Better conversions are obtained when $[Pt(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ reacts with Br_2 (1:1 molar ratio) or BrC_6F_5 (excess) to give $[Pt(C_6F_5)_2(Ph_2PCHBrPPh_2)]$ (**8b**) as the only reaction product. Moreover, $[Pd(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ reacts with I_2 (1:1 molar ratio) or IC_6F_5 (excess) to give $[Pd(C_6F_5)_2(Ph_2PCHIPPh_2)]$ (**9a**) in good yield, and the reaction between $[Pt(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ and I_2 (1:1 molar ratio) also gives the iodine derivative $[Pt(C_6F_5)_2(Ph_2PCHIPPh_2)]$ (**9b**) in good yield.

Other attempted halogenation reactions did not give such successful results: the reaction of $[Pd(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ with Cl_2, Br_2, or BrC_6F_5 results in the formation of a complex mixture of species, which we have not characterized. On the other hand, the reaction between $[M(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ (M = Pd, Pt) and C_6F_6, under the same conditions as those used with BrC_6F_5, gives $[M(C_6F_5)_2(Ph_2PCH_2PPh_2)]$ as the only identified product, with the protonation having occurred during the workup. This behavior can be explained by taking into account the fact that the reaction occurs through a simple metal−halogen exchange, similar to that used in the preparation of several organolithium compounds,[9] and the nature of the reactants. Here, we clearly see the lesser nucleophilic character of the palladium complexes compared to that of the platinum ones[10] (the anionic Pt derivative reacts with Cl_2 while the Pd one does not). On the other hand, the increasing strength of the halogen−halogen bond ($I_2 < Br_2 < Cl_2$) and that of the halogen−carbon bond ($I{-}C_6F_5 < Br{-}C_6F_5 < F{-}C_6F_5$) also play an important role: **7b** is obtained but with low conversion, while good yields of **8b** or **9b** are obtained.

Complexes **7b**−**9b** show similar spectroscopic features: the $^{31}P\{^1H\}$ NMR spectra (see Table 1) show a single resonance strongly shifted downfield with respect to the starting products as a result of the substitution of H by the more electronegative halogen atom. Similarly, the methine P_2CHX resonance appears in the ^{1}H NMR spectra as a triplet at higher frequency (about 2 ppm) than the P_2CH_2 hydrogens in the corresponding precursors. The ^{19}F NMR spectra also show similar characteristics for all complexes and will be discussed later. As in the preceding cases, these NMR data show that halogenation has occurred selectively at the methanide center. Similar halogen−halogen bond cleavages have been reported[6] for $[Mn(CO)_4(Ph_2PCHPPh_2)]$, which

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(10) This lesser nucleophilic character can be shown, for instance, by the different reactivities of anionic palladium and platinum complexes toward electrophilic substrates; some examples are given in refs 8 and 12.

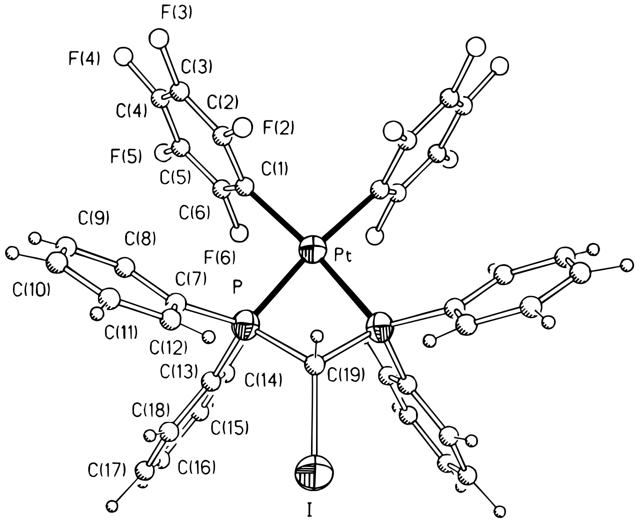

Figure 1. ORTEP representation of the molecular structure of complex **9b**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 9b

Pt−C(1)	2.067(5)	Pt−P	2.276(2)
I−C(19)	2.133(7)	P−C(13)	1.803(5)
P−C(7)	1.807(5)	P−C(19)	1.858(5)
C(19)−H(19)	0.93(8)		
C(1)#1−Pt−C(1)[a]	88.2(3)	C(1)−Pt−P#1	172.80(13)
C(1)−Pt−P	98.82(14)	P#1−Pt−P	74.09(7)
C(13)−P−C(7)	104.4(2)	C(13)−P−C(19)	111.3(3)
C(7)−P−C(19)	109.1(3)	C(13)−P−Pt	116.5(2)
C(7)−P−Pt	122.3(2)	C(19)−P−Pt	92.6(2)
C(2)−C(1)−Pt	120.9(4)	C(6)−C(1)−Pt	124.3(4)
C(12)−C(7)−P	124.7(5)	C(8)−C(7)−P	116.5(5)
C(14)−C(13)−P	119.0(4)	C(18)−C(13)−P	121.5(4)
P#1−C(19)−I	121.3(2)	P−C(19)−I	121.3(2)
P−C(19)−H(19)	100(3)	I−C(19)−H(19)	115(5)

[a] Symmetry transformations used to generate equivalent atoms. #1: $x, -y + {}^1/_2, z$.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 9b[a]

	x	*y*	*z*	*U*(eq)
Pt	510(1)	2500	4797(1)	34(1)
I	167(1)	2500	9444(1)	65(1)
P	397(1)	3184(1)	6483(1)	36(1)
C(1)	651(5)	3218(2)	3436(5)	38(1)
C(2)	1916(6)	3460(3)	3408(6)	53(1)
C(3)	2088(6)	3917(3)	2487(7)	62(2)
C(4)	947(6)	4144(3)	1531(6)	56(2)
C(5)	−346(6)	3923(3)	1531(5)	53(1)
C(6)	−465(5)	3462(3)	2464(5)	44(1)
F(2)	3081(3)	3258(2)	4330(4)	88(1)
F(3)	3367(4)	4129(2)	2491(5)	102(2)
F(4)	1107(4)	4564(2)	610(4)	87(1)
F(5)	−1473(4)	4137(2)	589(3)	82(1)
F(6)	−1773(3)	3260(2)	2385(3)	71(1)
C(7)	1589(5)	3873(2)	7034(5)	44(1)
C(8)	1477(8)	4397(3)	6157(8)	72(2)
C(9)	2362(10)	4943(4)	6510(11)	90(3)
C(10)	3346(9)	4963(4)	7718(11)	93(3)
C(11)	3465(9)	4452(4)	8561(10)	104(3)
C(12)	2588(8)	3902(4)	8222(7)	74(2)
C(13)	−1294(5)	3527(2)	6391(5)	41(1)
C(14)	−2410(5)	3383(3)	5300(5)	47(1)
C(15)	−3692(6)	3656(4)	5213(7)	65(2)
C(16)	−3898(7)	4067(4)	6177(8)	72(2)
C(17)	−2803(7)	4207(3)	7255(7)	69(2)
C(18)	−1490(7)	3946(3)	7375(6)	57(2)
C(19)	869(8)	2500	7720(7)	36(2)
C(20)	4923(28)	2500	7484(24)	185(11)
C(21)	5503(23)	2500	8756(25)	194(10)
C(22)	4433(9)	2500	9443(9)	60(2)
C(23)	5095(25)	2500	10676(28)	240(13)
C(24)	4441(28)	2500	11578(20)	214(12)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

can be halogenated to give $[Mn(CO)_4(Ph_2PCHXPPh_2)]^+$ and subsequently $[Mn(CO)_4(Ph_2PCXPPh_2)]$ and $[Mn(CO)_4(Ph_2PCX_2PPh_2)]^+$. These reactions are, as in our case, noteworthy because of their chemoselectivity and the fact that no side reactions (such as oxidations) are observed. For instance, oxidation processes take place when the free anions $Li[E(PPh_2)_2]$ (E = CH, N) react with I_2, giving interesting P−P or P−C coupling products, but in no case has the product of direct iodination been detected.[11]

The X-ray crystal structure of compound $\mathbf{9b}\cdot C_5H_{12}$ has been determined. Suitable crystals of $\mathbf{9b}\cdot C_5H_{12}$ were obtained by slow diffusion of petroleum ether into a CH_2Cl_2 solution of **9b** at −18 °C. A drawing of the structure is presented in Figure 1. Selected bond distances (angstroms) and angles (degrees) are collected in Table 3. Positional parameters and their estimated standard deviations are listed in Table 4.

The molecular structure involves the packing of two discrete monomeric molecules in the unit cell, which belongs to the centrosymmetric space group $P2_1/m$. Thus, the molecule has an imposed crystallographic symmetry of *m*; the platinum center, the methanide CH, and the iodine atom lie in the mirror plane. The platinum atom is located in a distorted square planar environment formed by the two C_{ipso} atoms of the C_6F_5 groups and the two phosphorus atoms of the chelate $Ph_2PCH(I)PPh_2$ ligand. The Pt−C(1) and Pt−P(1) bond distances (2.067(5) and 2.276(2) Å, respectively) are similar to distances found in other pentafluoro-[12] and dppm-containing[13] platinum complexes. The P(1)−Pt−P(1′) (74.09(7)°) and P(1)−C(19)−P(1′) (95.2(3)°) angles are reduced significantly from the usual normal bond angles of 90° and 109°, due to the strain in the chelate ring arising from the small bite of the phosphine ligand, and these angles are typical for chelating dppm.[1a,b,14] The P(1)−C(19) [P−CH(I)] distance (1.858(5) Å) is longer than other P−C(Ph) distances found in the same molecule (1.803(5), 1.807(5) Å) and is also typical for chelating dppm, showing that no double-bond character remains in these bonds. The C(19)−I(1) distance (2.133(7) Å) is longer than that in iodoarenes[15] and the angles around C(19) average 111.3°, which is close to the 109.5° expected for sp^3 hybridization, although the two independent angles are very different from each other (i.e., P(1)−C(19)−P(1′) = 95.2(3)°; P(1)−C(19)−I(1) = 121.3(2)°). On the other hand, the MP_2C ring is appreciably bent, with the carbon atom C(19) lying 0.52(1) Å out of the Pt−P(1)−P(1′) plane. Moreover, this bending is produced in such a way that the iodine atom is directed to the less sterically crowded position (opposite the platinum atom position).

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Reaction of $[Pt(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ with C_6F_5CN. In the preceding section we discussed the lack of reactivity between $[M(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ and C_6F_6, in which C−F bond cleavage does not take place. However, some examples of C−F bond cleavage in fluoroarenes C_6F_5X (especially those containing electron-withdrawing substituents X such as CN or NO_2) have been reported in the literature.[16] This cleavage is always produced by attack on the arene by a strong nucleophile through an aromatic nucleophilic substitution process. These aromatic nucleophilic substitutions are favored by the presence of the CN or NO_2 groups due to their ability to stabilize the intermediate species. In following that, we have attempted reactions between $[M(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ (M = Pd, Pt) and C_6F_5CN. While the palladium derivative does not react, $[Pt(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ reacts with C_6F_5CN to give the neutral derivative $Pt(C_6F_5)_2[Ph_2PCH(C_6F_4CN\text{-}4)PPh_2]$ (**10b**) as a result of C−F bond cleavage at the para position. This process is similar to that observed by Vicente et al.[16] in the reaction between C_6F_5CN and phosphine ylides. The spectroscopic data are in accord with the proposed structure (see Scheme 1). The IR spectrum of **10b** shows an intense absorption at 2222 cm^{-1}, demonstrating the presence of the C≡N group, and the ^1H NMR spectrum (see Table 1) shows the methine $P_2CH(C_6F_4CN)$ resonance as a triplet at 6.53 ppm, which is strongly shifted downfield (2.5 ppm) with respect to P_2CH_2 due to the high electron-withdrawing ability of the C_6F_4CN group. The $^{31}P\{^1H\}$ NMR spectrum (Table 1) shows a single resonance with ^{195}Pt satellites also shifted to low field (up to 25 ppm) with respect to the starting compund (see below for ^{19}F NMR discussion).

^{19}F NMR Spectra of Complexes 2a−10b. All complexes studied show similar characteristic features (see Table 2): at room temperature they show three sets of signals of relative intensity 2:1:2, corresponding to F_o, F_p, and F_m and in keeping with the presence of two equivalent C_6F_5 groups in which both halves of each C_6F_5 group act as equivalent AA′MM′X systems (the coordination plane is a symmetry plane on the NMR time scale). At −90 °C the signal due to F_o is split into two signals and the signal due to F_m is considerably broadened, but not totally split. This shows that at low temperatures the two halves of each C_6F_5 group are not equivalent (AFMRX system), as expected for a static structure (the coordination plane is not a symmetry plane).

A sensible explanation for these facts, taking into account the ^1H and $^{31}P\{^1H\}$ NMR discussion (see above), is the assumption of the free rotation of the *cis*-C_6F_5 groups around the $M-C_{ipso}$ bond at room temperature, a process that will be stopped at low temperature. In this respect, a temperature of −90 °C is needed for the complete splitting of the F_o signal in complexes with small groups at the methanide center (Me, Et, I, Br), while for the heterobimetallic derivatives **5a**−**6b** with bulky substituents at the methanide center, the splitting is observed at higher temperatures (around −30 °C, the steric crowding seems to be important). Moreover, in each pair of complexes Pd/Pt (i.e., **2a**/**2b** or **5a**/**5b**), we observe the same temperature dependence of the ^{19}F NMR spectra, so that there is no influence of the metal center in the coalescence process. Similar behavior has been found by us in the closely related complexes $M(C_6F_5)_2[(PPh_2)_2CH(PPh_2)]$ (M = Pd, Pt).[17] These data are in contrast with the general assumption of the hindered rotation of the *cis*-C_6F_5 groups around the $M-C_{ipso}$ bond,[18] but we have not found another sensible explanation for our results.

Finally, the ^{19}F NMR spectrum of complex **10b** shows, at room temperature, the presence of the resonances corresponding to the organometallic C_6F_5 groups (AA′MM′X system) together with two other resonances: a broad one at −130.20 ppm and a sharp doublet at −130.92 ppm, corresponding to the C_6F_4CN group. Upon cooling (−90 °C), the resonance of the organometallic F_o splits into two signals and the resonances of the C_6F_4CN group split into four well-resolved peaks corresponding to the four chemically inequivalent F atoms of the C_6F_4CN-4 unit. This seems to imply the free rotation, at room temperature, of the C_6F_5 and C_6F_4-CN-4 groups.

Conclusion. The synthesis of the carbanionic derivatives $[M(C_6F_5)_2(Ph_2PCHPPh_2)]^-$ (M = Pd, Pt) is accomplished by deprotonation of $[M(C_6F_5)_2(Ph_2PCH_2PPh_2)]$ with a strong base such as LDA or ^tBuLi. These complexes behave as strong nucleophiles and can be alkylated, metalated, or halogenated chemoselectively at the methanide carbon atom. The more nucleophilic platinum derivative can also promote *p*-C−F bond cleavage in functionalized fluoroarenes C_6F_5X (X = CN) as a result of an aromatic nucleophilic substitution process. An important feature of these ligands is their potential use as starting materials for the synthesis of a variety of diphosphines. In this respect, the displacement of the coordinated diphosphine from the metal center is the final step of complete metal-mediated synthesis of functionalized diphosphines. We are currently investigating this field.

Experimental Section

All compounds were prepared under a dry nitrogen atmosphere by using conventional vacuum line techniques. Solvents were dried and distilled prior to use by standard methods. Elemental analyses were carried out on a Perkin-Elmer 240-B microanalyzer. IR spectra (4000−200 cm^{-1}) were recorded from Nujol mulls on a Perkin-Elmer 883 spectrophotometer. ^1H NMR spectra were recorded at 300.13 MHz from $CDCl_3$ solutions (room temperature) on a Bruker ARX-300 spectrometer using the solvent signal as internal standard. ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded at 284.20 and 121.49 MHz, respectively, from $CDCl_3$ (room temperature) or CD_2Cl_2 solutions (^{19}F at −90 °C) on a Bruker ARX-300 spectrometer and referenced to $CFCl_3$ and H_3PO_4 (85%), respectively. *tert*-Butyllithium (1.7 M ^tBuLi solution in pentane) and lithium diisopropylamide (LDA, 2.0 M solution in heptane/THF/ethylbenzene) were obtained from commercial sources. The starting compounds *cis*-$M(C_6F_5)_2(Ph_2PCH_2PPh_2)$ [M = Pd (**1a**), Pt (**1b**)][19] and $ClAuPPh_3$[20] were prepared as previously reported.

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Synthesis of *cis*-M(C_6F_5)$_2$[$Ph_2PCH(Me)PPh_2$] [M = Pd (2a), Pt (2b)]. To a solution of **1a** (0.315 g, 0.382 mmol) in 10 mL of dry THF was added LDA (0.23 mL, 0.46 mmol). A clear yellow solution was obtained instantaneously. This solution was stirred for 5 min at room temperature, and then MeI (0.12 mL, 1.9 mmol) was added. The resulting pale yellow solution was stirred overnight and the solvent was evaporated to dryness; the residue was extracted with CH_2Cl_2 (30 mL) and filtered. Evaporation of the resulting colorless solution to small volume (≈2 mL) and addition of ^{i}PrOH (10 mL) produced the precipitation of a white solid, which was filtered, washed with *n*-hexane (10 mL), dried *in vacuo*, and identified by NMR spectroscopy as a mixture of **2a** and **3a** (0.25 g). Compound **2a** could be obtained in pure form by recrystallization from CH_2Cl_2/*n*-hexane: 0.211 g (65% yield). Anal. Calcd for $C_{38}H_{24}P_2F_{10}Pd$ (838.94): C, 54.40; H, 2.88. Found: C, 54.11; H, 2.77.

cis-Pt(C_6F_5)$_2$[$Ph_2PCH(Me)PPh_2$] (**2b**) was obtained in a similar way: **1b** (0.25 g, 0.27 mmol) was reacted with ^{t}BuLi (0.19mL, 0.32 mmol) and MeI (0.17 mL, 2.7 mmol) to give a mixture of **2b** and **3b** (0.20 g), from which **2b** [0.182 g (72% yield)] could be obtained in pure form after recrystallization. Anal. Calcd for $C_{38}H_{24}P_2F_{10}Pt$ (927.63): C, 49.20; H, 2.60. Found: C, 48.93; H, 2.51.

Reaction of *cis*-[M(C_6F_5)$_2$($Ph_2PCHPPh_2$)]$^-$ (M = Pd, Pt) with EtI. To a solution of **1a** (0.250 g, 0.303 mmol) in 10 mL of dry THF was added LDA (0.2 mL, 0.4 mmol). After 5 min, EtI (0.12 mL, 1.5 mmol) was added, and the resulting pale yellow solution was stirred overnight at room temperature. The solvent was then evaporated to dryness, and the residue was extracted with CH_2Cl_2 (30 mL) and filtered. The resulting colorless solution was evaporated to dryness, and the residue was treated with ^{i}PrOH (10 mL), giving a white solid (0.215 g) identified by NMR as a mixture of **1a** and **4a** in a 1:1.2 molar ratio. The reaction between **1b** (0.250 g, 0.274 mmol), ^{t}BuLi (0.19 mL, 0.32 mmol), and EtI (0.22 mL, 2.74 mmol), carried out similarly to that for **1a**, also gives a white solid (0.172 g), identified as a mixture of **1b** and **4b** (1:1.4 molar ratio).

Complexes **4a** and **4b** could not be obtained in analytically pure form due to the presence of the starting products. Attempts to separate these mixtures by fractional crystallization failed, always giving mixtures with the same (or nearly the same) composition as that of the starting mixture.

Synthesis of *cis*-M(C_6F_5)$_2$[$Ph_2PCH(M'PPh_3)PPh_2$] [M′ = Au, M = Pd (5a), Pt (5b); M′ = Ag, M = Pd (6a), Pt (6b)]. To a solution of **1a** (0.250 g, 0.303 mmol) in 15 mL of dry THF at room temperature was added LDA (0.2 mL, 0.4 mmol), giving a yellow solution. After 5 min of stirring at room temperature, $ClAuPPh_3$ (0.150 g, 0.303 mmol) was added and the resulting pale yellow solution was stirred for 1 h. The solvent was then evaporated to dryness and the residue was treated with 20 mL of anhydrous Et_2O. The small quantity of the remaining solid was filtered, and the resulting solution was evaporated to a small volume (≈2 mL). Addition of *n*-hexane (20 mL) produced the precipitation of a pale yellow solid (**5a**), which was filtered and dried *in vacuo*: 0.388 g (87% yield). Anal. Calcd for $C_{55}H_{36}P_3F_{10}PdAu$ (1283.16): C, 51.48; H, 2.83. Found: C, 51.37; H, 3.02.

cis-Pt(C_6F_5)$_2$[$Ph_2PCH(AuPPh_3)PPh_2$] (**5b**) was obtained similarly, as a white solid, by using **1b** (0.250 g, 0.274 mmol), ^{t}BuLi (0.19 mL, 0.32 mmol), and $ClAuPPh_3$ (0.135 g, 0.274 mmol): 0.262 g (70% yield). Anal. Calcd for $C_{55}H_{36}P_3F_{10}PtAu$ (1371.85): C, 48.15; H, 2.64. Found: C, 48.06; H, 2.50.

cis-Pd(C_6F_5)$_2$[$Ph_2PCH(AgPPh_3)PPh_2$] (**6a**) was obtained similarly by starting from **1a** (0.250 g, 0.303 mmol), LDA (0.20 mL, 0.40 mmol), and $O_3ClOAgPPh_3$ (0.142 g, 0.303 mmol), resulting in a white solid. The product was recrystallized from CH_2Cl_2/*n*-hexane, giving **6a** as a CH_2Cl_2 solvate: 0.210 g (58% yield). The amount of CH_2Cl_2 was determined by ^{1}H NMR. Anal. Calcd for $C_{55}H_{36}P_3F_{10}PdAg{\cdot}0.3CH_2Cl_2$ (1219.54): C, 54.46; H, 3.02. Found: C, 54.38; H, 3.17.

cis-Pt(C_6F_5)$_2$[$Ph_2PCH(AgPPh_3)PPh_2$] (**6b**) was obtained similarly, as a white solid, starting from **1b** (0.250 g, 0.274 mmol), ^{t}BuLi (0.19 mL, 0.32 mmol), and $O_3ClOAgPPh_3$ (0.129 g, 0.274 mmol). The product was recrystallized from CH_2Cl_2/*n*-hexane, giving **6b** as a CH_2Cl_2 solvate: 0.155 g (44% yield). The amount of CH_2Cl_2 was determined by ^{1}H NMR. Anal. Calcd for $C_{55}H_{36}P_3F_{10}PtAg{\cdot}0.3CH_2Cl_2$ (1308.23): C, 50.77; H, 2.82. Found: C, 50.51; H, 3.06.

Reaction of *cis*-[Pt(C_6F_5)$_2$($Ph_2PCHPPh_2$)]$^-$ with Cl_2. A solution of **1b** (0.120 g, 0.131 mmol) in 15 mL of dry THF at room temperature was treated with ^{t}BuLi (0.10 mL, 0.17 mmol) and subsequently with a solution of Cl_2 in CCl_4 (0.60 mL, 0.14 mmol). The reaction mixture was stirred for 6 h at room temperature and then evaporated to dryness. The residue was extracted with CH_2Cl_2 (30 mL) and filtered, and the solution was evaporated to dryness. The resulting white residue was washed with *n*-hexane (10 mL) and dried *in vacuo*, affording 0.090 g of a white solid that was identified by NMR spectroscopy as a mixture of **1b** and **7b** in a 9:1 molar ratio.

Synthesis of *cis*-Pt(C_6F_5)$_2$[$Ph_2PCH(Br)PPh_2$] (8b). (a) To a solution of **1b** (0.250 g, 0.274 mmol) in 20 mL of dry THF was added LDA (0.17 mL, 0.34 mmol), and after 5 min of stirring at room temperature, BrC_6F_5 (0.18 mL, 1.37 mmol) was added. The resulting pale yellow solution was stirred for 24 h at room temperature and then refluxed for an additional 2 h. After cooling, the solvent was evaporated to dryness, and the remaining residue was extracted with anhydrous Et_2O (20 mL). The solid in suspension was filtered, the ether solution was evaporated to a small volume (≈2 mL), and *n*-hexane (20 mL) was added, resulting in the precipitation of a white solid (**8b**), which was filtered and vacuum-dried: 0.123 g (45% yield).

(b) To a solution of **1b** (0.250 g, 0.274 mmol) in 15 mL of dry THF was added ^{t}BuLi (0.17 mL, 0.30 mmol), and after 5 min of stirring at room temperature, Br_2 in CCl_4 (1.47 mL, 0.28 mmol) was added. The resulting pale yellow solution was stirred for 6 h at room temperature and then evaporated to dryness, and the residue was extracted with 20 mL of CH_2Cl_2. The remaining white solid was filtered and the clear solution was evaporated to a small volume (≈2 mL). Addition of Et_2O (5 mL) and hexane (15 mL) produced the precipitation of **8b**: 0.20 g (74% yield). Anal. Calcd for $C_{37}H_{21}F_{10}P_2BrPt$ (992.50): C, 44.77; H, 2.13. Found: C, 44.90; H, 2.48.

Synthesis of *cis*-M(C_6F_5)$_2$[$Ph_2PCH(I)PPh_2$] [M = Pd (9a), Pt (9b)]. (a) To a solution of **1a** (0.250 g, 0.303 mmol) in 15 mL of dry THF was added LDA (0.20 mL, 0.40 mmol), and subsequently IC_6F_5 was added (0.40 mL, 3.0 mmol). The resulting yellow solution was stirred at room temperature for 6 h and then refluxed for an additional 3 h and evaporated to dryness. The residue was extracted with 20 mL of CH_2Cl_2 and filtered, and the solution was evaporated to a small volume (2 mL). The addition of *n*-hexane (20 mL) produced the precipitation of a yellow orange solid (**9a**), which was filtered and air-dried: 0.151 g (53% yield).

(b) To a solution of **1a** (0.200 g, 0.242 mmol) in 15 mL of dry THF were added ^{t}BuLi (0.15 mL, 0.25 mmol) and, subsequently, I_2 (0.063 g, 0.25 mmol). The resulting yellow solution was stirred at room temperature for 6 h and then evaporated to dryness. The residue was extracted with 20 mL of CH_2Cl_2 and filtered, and the solution was evaporated to a small volume (≈2 mL). The addition of *n*-hexane (20 mL) produced the precipitation of **9a**: 0.169 g (74% yield). Anal. Calcd for $C_{37}H_{21}F_{10}P_2IPd$ (950.80): C, 46.74; H, 2.22. Found: C, 46.45; H, 2.06.

The complex *cis*-Pt(C_6F_5)$_2$[$Ph_2PCH(I)PPh_2$] (**9b**) was obtained, as a yellow crystalline solid, by following method b and starting from **1b** (0.250 g, 0.274 mmol), ^{t}BuLi (0.19 mL, 0.32 mmol), and I_2 (0.076 g, 0.30 mmol): 0.238 g (84% yield). Anal. Calcd for $C_{37}H_{21}F_{10}P_2IPt$ (1039.49): C, 42.75; H, 2.03. Found: C, 42.61; H, 1.99.

Synthesis of *cis*-Pt(C_6F_5)$_2$[$Ph_2PCH(p\text{-}C_6F_4C{\equiv}N)PPh_2$] (10b). To a solution of **1b** (0.250 g, 0.274 mmol) in 15 mL of dry THF was added LDA (0.2 mL, 0.4 mmol). The resulting yellow solution was stirred for 15 min at room temperature and then treated with $C_6F_5C{\equiv}N$ (0.35 mL, 2.7 mmol). The red solution obtained was refluxed for 3.5 h and then cooled and evaporated to dryness. The residue was extracted with CH_2Cl_2 (20 mL), filtered (a small quantity of a gray solid was discarded), and again evaporated to dryness. A new extraction with anhydrous Et_2O (20 mL) produced the precipitation of a small amount of starting product **1b** which was also discarded. The clear ether solution was evaporated to dryness and the oily residue was treated with *n*-hexane, giving a pale orange solid that was filtered and dried *in vacuo*. Subsequent recrystallization from $CHCl_3$/*n*-hexane afforded white crystals of **10b**: 0.15 g (50% yield). Anal. Calcd for $C_{44}H_{21}F_{14}P_2NPt$ (1086.67): C, 48.63; H, 1.94; N, 1.29. Found: C, 48.52; H, 2.01; N, 1.44.

X-ray Data Collection, Structure Determination, and Refinement for $[Pt(C_6F_5)_2(Ph_2PCHIPPh_2)]\cdot C_5H_{12}$ (9b·C_5H_{12}). A pale yellow crystal of **9b**·C_5H_{12} (approximate dimensions 0.47 × 0.41 × 0.40) was mounted on a glass fiber and covered with epoxy. The crystallographic data are summarized in Table 5. All diffraction measurements were made at room temperature with an automated four-circle diffractometer.[21] Although the lattice parameters emerged from routine procedures without difficulty, axial photographs were taken of the *a*-, *b*-, and *c*-axes to verify the lattice dimensions. The diffraction spots were broad and poorly shaped. Unit cell dimensions were determined from 25 centered reflections in the range $21.9 \le 2\theta \le 31.6°$. For intensity data collection, ω scans were used with $\Delta\omega = 1.25 + 0.35 \tan \theta$. Three check reflections remeasured after every 3 h of beam time showed a decay of not more than 2% over the period of data collection. An empirical absorption correction was based on 518 azimuthal scan data (maximum and minimum transmission coefficients were 1.000 and 0.769).[22] The structure was solved and developed by Patterson and Fourier methods. All non-hydrogen atoms were assigned anisotropic displacement parameters. The hydrogen atoms were located in a final difference Fourier map and refined with isotropic thermal displacement parameters. Five atomic sites in an interstitial zone, with each mean atomic position lying on a crystallographic mirror, were modeled as a C_5H_{12} molecule with anisotropic displacement parameters for the five carbon atoms. The parameters for the interstitial pentane moiety, not surprisingly, showed signs of either static or dynamic disorder. That is, the bond distances are shorter than the known values for C−C bonds, and the displacement parameters for the atoms of both terminal C_2H_5 groups are large and quite anisotropic. The hydrogen atoms of this group were omitted from the model. The data to parameter ratio in the final refinement was 12.7. The structure was refined to F_o^2, and all reflections were used in the least-squares calculations.[23]

Table 5. Crystal Data and Structure Refinement for 9b

identification code	$[Pt(C_6F_5)_2(Ph_2PCHIPPh_2)]\cdot C_5H_{12}$
empirical formula	$C_{42}H_{33}F_{10}IP_2Pt$
formula weight	1111.61
temperature (K)	293(2)
wavelength (Å)	0.710 73
crystal system	monoclinic
space group	$P2_1/m$
unit cell dimensions	$a = 10.011(7)$ Å, $\alpha = 90°$ $b = 20.038(9)$ Å, $\beta = 106.84(4)°$ $c = 10.559(5)$ Å, $\gamma = 90°$
volume (Å^3)	2027(2)
Z	2
density (calculated) (Mg/m^3)	1.821
absorption coefficient (mm^{-1})	4.377
$F(000)$	1072
crystal size (mm)	0.47 × 0.41 × 0.40
θ range for data collection (deg)	2.02−24.97
index ranges	$0 \le h \le 11$, $0 \le k \le 23$, $-12 \le l \le 12$
reflections collected	3899
independent reflections	3671 ($R_{int} = 0.0158$)
absorption correction	psi
max and min transmission	1.000 and 0.769
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	3671/0/308
goodness-of-fit on F^2	1.060
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0298$, $wR_2 = 0.0745$
R indices (all data)	$R_1 = 0.0376$, $wR_2 = 0.0790$
largest diff. peak and hole (e Å^{-3})	0.750 and −0.990

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Supporting Information Available: Tables of complete bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates for **9b** (7 pages). Ordering information is given on any current masthead page.

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(21) Diffractometer control program: CAD4.PC Version 1.5c, Delft Instruments X-ray Diffraction bv, Delft, The Netherlands, 1994.

(22) Data were processed on a local area VAXCluster (VMS V5.5-2) with the commercial package SHELXTL-Plus Release 4.21/V, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990.

(23) (a) Sheldrick, G. M. Shelxl-93: Fortran-77 program for the refinement of crystal structures from diffraction data, University of Göttingen, 1993. (b) Sheldrick, G. M., in preparation.