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Reactivity of electrophilic palladium alkyl cations stabilized by electron-rich chelating diphosphine ligands. Evidence for dinuclear intermediates and the formation of a dinuclear mixed-valence methyl cation ‡

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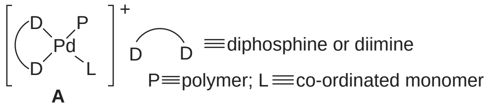
The reactivity of the electron-rich palladium alkyl cation, $[Pd(dippe)R]^+BAr_4^-$ (dippe = 1,2-bis(diisopropylphosphino)ethane; R = η^3-CH_2Ph or CH_3; BAr_4 = $\{B[3,5-(F_3C)_2C_6H_3]_4\}$) with a variety of small molecules is reported. Although the benzyl cation is unreactive towards carbon monoxide and dihydrogen, the corresponding methyl cation, $[Pd(dippe)Me(s)]^+$ (s = Et_2O, THF or *o*-dichlorobenzene) reacts rapidly with H_2 to produce the dihydride-bridged dimer $\{[(dippe)Pd]_2(\mu\text{-}H)_2\}^{2+}$, and with CO to produce the dinuclear mixed-valence, cationic complex $[Pd(dippe)(\mu\text{-}CO)Pd(dippe)Me][BAr_4]$. In addition, the methyl cation can abstract alkyl groups from neutral dialkyl complexes; thus, the addition of $[Pd(dippe)Me(s)]^+$ to $Pd(dippe)(CH_2Ph)_2$ results in the formation of the methyl benzyl derivative $Pd(dippe)Me(CH_2Ph)$ and the cationic benzyl cation $[Pd(dippe)(\eta^3\text{-}CH_2Ph)]^+$. Methyl group interchange is also observed for the reaction of the methyl cation with the neutral dimethyl; when $[Pd(dippe)Me(s)]^+$ is mixed with $Pd(dippe)(^{13}CH_3)_2$, the carbon-13 label is immediately scrambled to the cation. These exchange reactions are suggested to occur *via* dinuclear intermediates. The mixed-valence dinuclear species mentioned above has been investigated in some detail; mechanistic studies have indicated that the addition of CO to $[Pd(dippe)Me(s)]^+$ probably proceeds *via* simple substitution of the solvent by CO to generate the expected mononuclear methyl carbonyl cation $[Pd(dippe)Me(CO)]^+$, followed by migratory insertion to give the acetyl carbonyl derivative $[Pd(dippe)(COMe)(CO)]^+$. The final product is the dinuclear mixed-valence species $[Pd(dippe)(\mu\text{-}CO)Pd(dippe)Me][BAr_4]$, which is accompanied by the formation of acetone (Me_2CO) and the dicarbonyl dication $[Pd(dippe)(CO)_2]^{2+}$. Presumably, methyl transfer occurs at some stage from the methyl cation to generate the methyl–acetyl complex, Pd(dippe)Me(COMe); reductive elimination of acetone under CO from the methyl–acetyl complex produces the Pd^0 complex Pd(dippe)CO which then reacts with the starting methyl cation to generate the dinuclear mixed-valence species. Addition of CO to the mixed-valence species does not result in formation of mononuclear complexes, rather 1 equivalent of CO adds to form a new dinuclear complex with two bridging COs.

Soluble palladium complexes are widely used as catalysts for many organic transformations.[1,2] Recently, cationic Pd^{II} derivatives have come under intense scrutiny as catalysts for the copolymerization of carbon monoxide and olefins, and for the polymerization of functionalized olefins.[3–19] In both of these processes, one of the propagating species is believed to consist of a cationic square-planar derivative (**A**) stabilized by a bidentate chelating ligand, usually a diphosphine or a diimine, with the other two sites occupied by monomer and growing polymer.[20]



A

From a design point of view, such a configuration would appear ideal since the chelating ancillary ligand restricts the two reactive sites to be *cis* disposed, exactly as required for the migratory insertion type reaction.[21] In addition, the steric and electronic properties of the ancillary ligand can be varied to influence the stereochemistry and molecular weight of the resulting polymers.[5]

In this paper we report the stoichiometric reactivity of electrophilic palladium(II) alkyl cations with small molecules such as H_2 and CO and make comparisons with the neutral dialkyl analogues. What we find is that the reactivity of these cations is generally enhanced as compared with their neutral counterparts, and that dinuclear products and intermediates play an important role in the chemistry of these species.

Results and Discussion

Preparation of cationic alkyls and hydrides of Pd^{II}

We have previously reported the preparation of dinuclear hydrides of palladium(I)[22] and catalytically active palladium(0)[23] complexes that incorporate electron-rich chelating ligands bearing isopropyl substituents, *i.e.* 1,2-bis(diisopropylphosphino)ethane (dippe) and 1,3-bis(diisopropylphosphino)propane (dippp). To prepare cationic alkyl complexes, we chose the method developed by Brookhart *et al.* involving protonation of neutral dialkyl complexes using $HBAr_4$ ($HBAr_4$ = $[H(OEt_2)_2]^+\{B[3,5-(F_3C)_2C_6H_3]_4\}^-$).[7] The starting dialkyl derivatives, $Pd(dippe)R_2$ and $Pd(dippp)R_2$ (where R = Me or CH_2Ph) are prepared *via* standard preparative routes as described in the Experimental section. Protonation of the dibenzyl complex $Pd(dippe)(CH_2Ph)_2$ leads to the formation of the η^3-benzyl derivative $[Pd(dippe)(\eta^3\text{-}CH_2C_6H_5)]^+BAr_4^-$ [equation (1)].

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **1** shows the required AX pattern due to inequivalent phosphorus nuclei, *i.e.* a pair of doublets at δ 88.7 and 75.2 ($J_{PP'}$ = 32.1 Hz), and the ^1H and $^1H\text{-}\{^{31}P\}$ NMR spectra are representative of an unsymmetrical complex. Of particular note are the four isopropyl methyl

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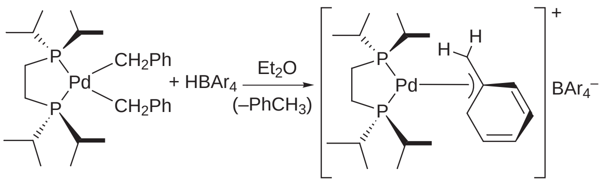
‡ *Non-SI units employed*: atm = 101 325 Pa; mmHg = 133.322 Pa.

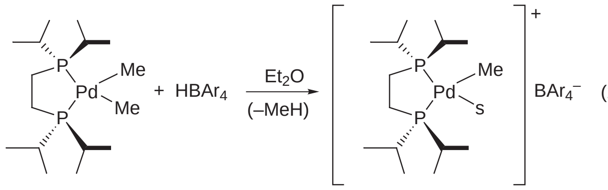


1 [BAr$_4$] (1)

signals between δ 1.07 and 0.75 and the two isopropyl methine resonances at δ 2.37 and 1.98; the ^{1}H-{^{31}P} NMR spectrum again shows the inequivalence of the methylene backbone of the ligand with the two triplets required for the A_2X_2 spin-system of the $CH_2CH'_2$ linkage. Significantly, signals due to the *ortho* protons of the benzyl group are observed at δ 6.41.[24] This upfield value indicates η^3-co-ordination and the assignment is further evidenced by an NOE experiment: irradiation of the benzylic protons results in signal enhancement of the peak at δ 6.41, due to the *ortho* protons, and a negative NOE with the *meta* protons at δ 7.3. The *ortho* and benzylic protons each appear as single multiplets in the ^{1}H NMR spectrum and their equivalence is maintained even at −90 °C, as is the inequivalence of the phosphorus nuclei in the ^{31}P-{^{1}H} NMR spectrum. This dynamic behaviour is consistent with a fast η^1–η^3 suprafacial shift of the palladium nucleus, which interchanges both *syn* and *anti* benzyl protons, and *ortho*-phenyl protons but maintains the non-equivalence of the phosphine donors.[25]

The preparation of the same benzyl cation **1** could also be effected by benzyl abstraction from the starting neutral derivative Pd(dippe)$(CH_2C_6H_5)_2$ by $B(C_6F_5)_3$, one of the Lewis acids that has been used in the synthesis of single-site olefin polymerization catalysts.[26] Although a 1:1 mixture of the two reagents generated an oil, the solution spectra of the product were equivalent to that of **1**, except for the benzylic signals due to $[B(C_6F_5)_3CH_2C_6H_5]^-$ observed in the ^{1}H NMR spectrum. The labeled derivative, **1**-d_7, was also prepared by protonation with $HBAr_4$ on Pd(dippe)$(CD_2C_6D_5)_2$ [prepared in turn from Pd(dippe)Cl_2 and 2 equivalents of $KCD_2C_6D_5$], and a doublet was observed at δ 2.30 (J_{HD} = 2.5 Hz) in the ^{2}H NMR spectrum of the reaction mixture due to extruded $HD_2CC_6D_5$.

Although cationic, the reactivity of [Pd(dippe)(η^3-$CH_2C_6H_5$)]$^+$ is unremarkable. Cation **1** is inert to both CO and H_2, and is in fact air-stable. This is not too surprising as examples of stable η^3-allyl palladium cations are legion, and their chemistry is mature.[27] We therefore chose to examine protonation reactions of Pd(dippe)Me_2 and Pd(dippp)Me_2. To an ethereal solution of either palladium dimethyl complex, the addition of 1 equivalent of $HBAr_4$ causes a rapid effervescence, undoubtedly of methane, and the methyl cations [Pd(dippe)Me(OEt_2)]$^+$ **2** and [Pd(dippp)Me(OEt_2)]$^+$ **3** are obtained as shown for **2**[BAr$_4$] in equation (2).

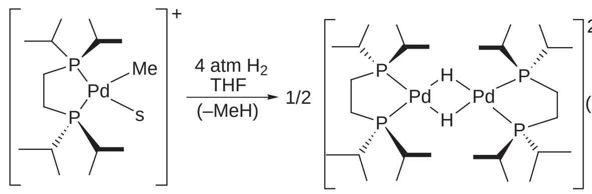


2[BAr$_4$] (s = Et_2O) (2)

Because the remaining methyl group bound to the Pd centre cannot offer additional π interaction as can an allyl or benzyl group, the metal nucleus is now highly electrophilic and is loosely stabilized by whatever solvent molecules are available. In different NMR solvents, or even an ethereal solution of the cation to which different solvents are successively added, this gives rise to a series of solution spectra which indicates the progressive filling of the vacant co-ordination site by the stronger donor. The ^{31}P-{^{1}H} NMR spectrum of **2** thus consists of an AX pattern and in different NMR solvents the chemical shift of the two doublets change noticeably. From a starting solution of Pd(dippe)Me_2 plus $HBAr_4$ in Et_2O–C_6D_6 the following ^{31}P-{^{1}H} NMR parameters can be generated: an AX pattern at δ 84.2 and 63.1 (J_{AX} = 17.4 Hz) due to [Pd(dippe)Me(OEt_2)]$^+$ **2a**; following addition of a few drops of THF, an AX pattern at δ 86.0 and 69.0 (J_{AX} = 17.0 Hz), due to [Pd(dippe)Me(THF)]$^+$ **2b**; and following addition of excess PPh_3, an AMX pattern at δ 78.3, 70.0 and 29.8 (J_{AX} = 368.0, J_{AM} = 21.9, J_{MX} = 29.5 Hz) due to [Pd(dippe)Me(PPh_3)]$^+$ **2c**. These data are in accord with a square-planar palladium cation whose fourth co-ordination site is filled by a labile solvent molecule. For this reason, we will refer to **2** as the cation [Pd(dippe)Me(s)]$^+$ where s is the reaction- or NMR-solvent.

Additional information can be obtained by examination of the ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra of the carbon-13 labelled species [Pd(dippe)^{13}Me(s)]$^+$ (**2**-$^{13}C_1$). The ^{31}P-{^{1}H} NMR spectrum of **2**-$^{13}C_1$ is an ABX pattern with two non-equivalent phosphorus nuclei ($J_{PP'}$ = 16.7 Hz) coupled to a single ^{13}C nucleus (J_{CP} = 86.1, $J_{CP'}$ = 2.8 Hz). The two values of $^2J_{CP}$ are again consistent with a *trans* and *cis* coupling respectively across a square-planar centre. The corresponding ^{13}C-{^{1}H} NMR spectrum exhibits an apparent doublet of doublets for the enriched methyl resonance due to the strong *trans* coupling and the *cis* coupling of much smaller magnitude (this splitting is not well resolved in the ^{31}P-{^{1}H} NMR spectrum). The non-ambiguous coupling constants and chemical shifts detailed above for the [Pd(dippe)Me]$^+$ system prove useful in monitoring the reactivity of this complex. As a sidebar, elemental analyses of the methyl cations **2** and **3** do not show evidence for the presence of co-ordinated solvent; presumably, in the solid state, the anion weakly co-ordinates enough so that the solvent can be removed by pumping under vacuum. Attempts to obtain X-ray quality crystals of these cations have failed thus far.

In the reactions with small molecules, the electrophilic methyl cation **2** shows enhanced reactivity as compared to the neutral precursor. For example, Pd(dippe)Me_2, the parent complex of **2**, is completely inert to dihydrogen. In contrast, a THF solution of **2**, placed under 1–4 atm of H_2, rapidly develops a red colour, the ^{31}P-{^{1}H} NMR spectroscopy reveals a singlet at δ 92.0, due to equivalent phosphorus donors. The corresponding ^{1}H NMR spectrum reveals a binomial quintet in the hydride region at δ −5.75 (J_{PH} = 55.0 Hz) indicative of rapid fluxional exchange similar to that found for the related neutral hydride dimers.[22] Solution spectroscopy therefore indicates that a dinuclear Pd species, {[(dippe)Pd]$_2$(μ-H)$_2$}[BAr$_4$]$_2$ **4**[BAr$_4$]$_2$, results from the activation of dihydrogen by **2**. As shown by the corresponding reaction between H_2 and [Pd(dippe)^{13}Me(s)]$^+$ (**2**-$^{13}C_1$) and the observation of $^{13}CH_4$ in solution, the methyl residue of **2** is lost as methane as shown in equation (3).

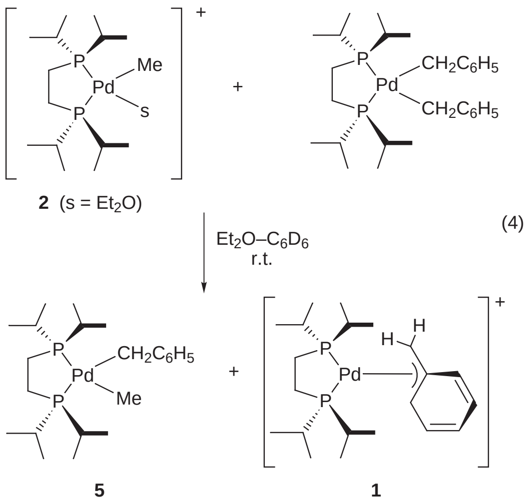


2 (s = THF) **4** (3)

The orientation of the bridging hydrides of **4**, shown to be planar in equation (3), is speculation at this point and is based on the propensity for four-co-ordinate, Pd^{II} systems to be square planar; however, other geometries[22] are certainly possible and cannot be ruled out.

With regards to the enhanced reactivity of the methyl cation **2** with H_2, it is interesting to note that the cationic nature of **2** is not a sufficient condition to augment reactivity since, as already mentioned, the 16-e benzyl cation **1** is also inert to H_2. Thus it would appear that the reactivity is a result of both co-ordinative unsaturation at the palladium centre and the positive charge, although it is difficult to rank the relative merit of either effect since they are intimately connected in these systems; neutral Pd^{II} systems with labile ligands would be the obvious targets to try to compare to these cationic systems.

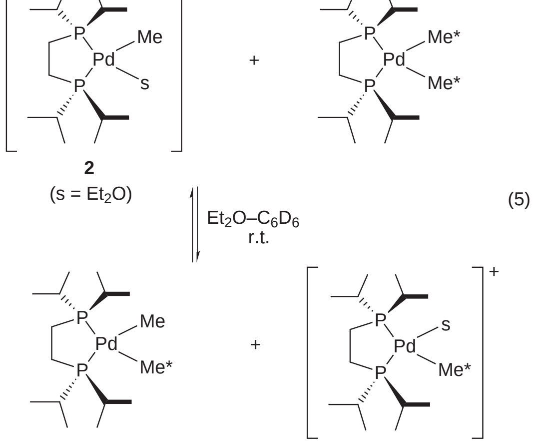
The electrophilicity of the palladium nucleus in **2** can also be demonstrated by the reaction of **2** with $Pd(dippe)(CH_2C_6H_5)_2$. The stoichiometric solution of methyl cation **2** and $Pd(dippe)(CH_2C_6H_5)_2$ in Et_2O–C_6D_6 leads to the formation of two products, of different solubility, both of which give rise to AX patterns in the ^{31}P-{^1H} NMR spectrum. The identity of the benzene insoluble but ether soluble product is the η^3-benzyl cation **1**, whereas the other product, which is soluble in benzene and displays both methyl and benzylic resonances in its ^1H NMR spectrum, was identified as $Pd(dippe)(Me)(CH_2C_6H_5)$ **5**. Complex **5** was unequivocally characterized by independent synthesis from Pd(dippe)MeCl and benzyl potassium. Evidently, the acidic palladium centre of **2** abstracts a benzyl group from $Pd(dippe)(CH_2C_6H_5)_2$ to give quantitative yields of the neutral, mixed hydrocarbyl complex, **5**, and the stabilized η^3-benzyl cation **1** [equation (4)].



(4)

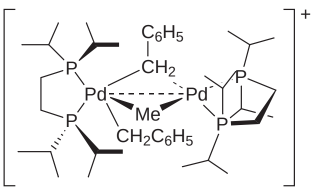
A potentially more interesting result occurs when an ethereal solution of **2** is mixed with 1 equivalent of its labelled parent molecule, $Pd(dippe)(^{13}CH_3)_2$. Hydrocarbyl transfer is again observed with the decrease in intensity of the second order $[AX]_2$ multiplet due to $Pd(dippe)(^{13}CH_3)_2$ in the ^{31}P-{^1H} or ^{13}C-{^1H} NMR spectra and the observation of simpler ABX patterns due to isotopomeric $[Pd(dippe)Me]^+$/$[Pd(dippe)Me^*]^+$ and $Pd(dippe)Me_2$/$Pd(dippe)MeMe^*$ [equation (5)].

It is clear that there is no thermodynamic driving force in this last reaction in that a more stable species such as the η^3-benzyl cation is not generated. It must simply be that the Lewis acidity of the palladium nucleus of **2** renders the complex exceptionally kinetically labile. Hydrocarbyl transfer was also observed in the reaction between $[Cp^*_2ZrCH_3]^+$ and $Cp^*_2Zr(^{13}CH_3)_2$, where the Zr nucleus was similarly Lewis-acidic, and the anion $[B(C_6F_5)_3Me]^-$, similarly poorly co-ordinating.[26]



(5)

2–^{13}C



B

In both reactions shown in equations (4) and (5) an intermediate cannot be observed in the ^{31}P-{^1H} NMR spectrum, and yet a hydrocarbyl residue has been demonstrably transferred from one Pd^{II} nucleus to another. In order to account for this process a dinuclear species, as an intermediate or transition state, must be invoked. One possibility is shown in **B**, in which the hydrocarbyl residues bridge both metal centres.

Reaction with carbon monoxide

As part of our interest in the reactivity of the electron-rich Pd^{II} methyl cation **2**, we examined its reaction with CO. Based on many model studies for palladium alkyl phosphine and diimine complexes,[11,28–32] one would predict that the sequence of reactions would involve CO first displacing the solvent molecule, then migratory insertion would occur to yield a Pd–acyl species, which would be trapped either by solvent or by CO. These acyl species are regarded as important intermediates in the copolymerization of CO and ethylene.[5,33] Moreover, this is simply an example of migratory insertion, which has long been recognized as a fundamental organometallic reaction pathway.[21] However, when a solution of **2** in [$^2H_8$]THF is placed under 1–4 atm of CO, instead of observing a new doublet of doublets in the ^{31}P-{^1H} NMR spectrum, as would be generated by the AX spin system of a $[Pd(dippe)(COMe)s]^+$ species (s = solvent molecule or CO), the major feature observed was a *singlet* at δ 58.7, indicating equivalence of the phosphorus donors of the dippe ligand, accompanied by the appearance of a deep orange colour for the solution. In addition, it was observed that this product remained stable under added pressure of CO (*i.e. ca.* 5 atm), and signals attributable to acyl groups could not be identified in the ^1H NMR spectrum. Under an atmosphere of ^{13}CO the ^{31}P-{^1H} NMR signal at δ 58.7 splits into a doublet of doublets ($J_{PC} = 28.1$; $J_{PC'} = 25.5$ Hz) and *quintet* absorptions with the same coupling constants were observed at low field in the ^{13}C-{^1H} NMR spectrum (δ 236.4 and 228.1 respectively). When the corresponding experiment was performed using **2**-$^{13}C_1$ under CO, the ^{31}P-{^1H} NMR spectrum revealed a doublet at δ 58.7 ($J_{PC} = 14.4$ Hz), and in the ^{13}C-{^1H} NMR spectrum a binomial *quintet* was observed at δ 47.3 ($J_{CP} = 14.6$ Hz). These results indicate the formation of some dinuclear palladium species that is bridged by two chemically different carbonyl groups and in which the four phosphorus donors are equivalent. However, as will be seen in the next section, the solid-state molecular structure required modification of this conclusion.

Solid-state and solution structure of [Pd(dippe)(μ-CO)Pd(dippe)-Me][BAr_4] 6[BAr_4]

Amber crystals from the reaction of **2** with CO were obtained from Et_2O–toluene. The structure is shown in Fig. 1; crystal data and selected bond lengths and angles are listed in Tables 1 and 2 respectively. Each palladium nucleus of **6** resides in a distinct co-ordination environment. The dipalladium core of **6** is monocationic, and the structure depicted is associated with a BAr_4 anion that is isolated from both palladium nuclei though

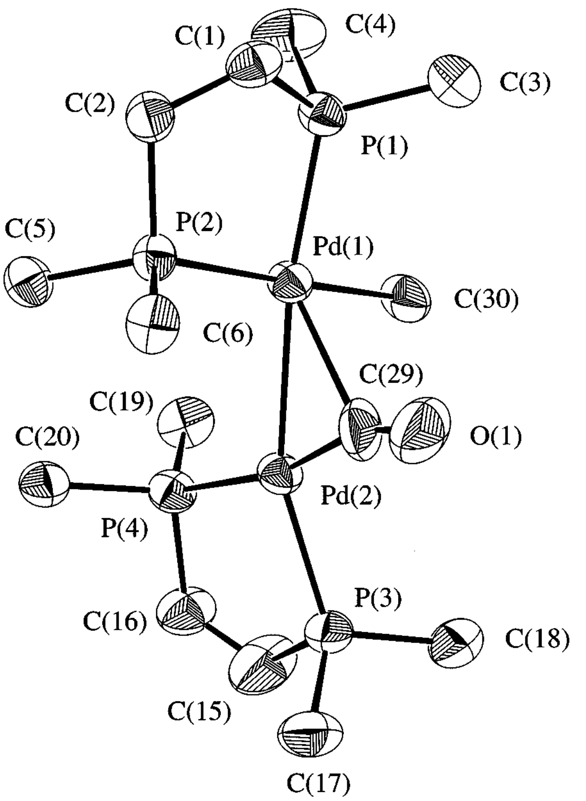


Fig. 1 Molecular structure and numbering scheme for the cation [Pd(dippe)(μ-CO)Pd(dippe)Me]$^+$ **6**

closer in space to Pd(1). In the cation, Pd(2) interacts with the carbonyl group with a Pd–C separation of 1.873(10) Å, meanwhile its interaction with C(30) of the methyl group is minimal; here the separation is 2.94(1) Å. On the other hand, Pd(1) is separated from C(29) by 2.32(1) Å, yet its distance of 2.172(7) Å from the methyl carbon, C(30), clearly indicates that the methyl group is covalently bound to this centre.[34] Given this non-symmetric bridging of the carbonyl group across the palladium centres, and the disposition of the methyl group, it is reasonable to formulate **6** as a mixed-valence species of Pd, that is, as an adduct of a basic Pd^0 complex, Pd(dippe)CO, and a Lewis-acidic Pd^{II} species, [Pd(dippe)Me]$^+$. Indeed, **6** could be reformulated as a conventional square-planar palladium co-ordination complex, with Pd(1) as the central metal atom and the Pd(dippe)CO moiety as the fourth ligand, if the relevant bond angles are considered. The angles P(2)–Pd(1)–C(30) and P(1)–Pd(1)–Pd(2) are tolerably close to 180° [177.7(2) and 170.32(6)° respectively], and the angles Pd(2)–Pd(1)–C(30) and P(1)–Pd(1)–C(30) [78.5(2) and 91.9(2)°] are reasonably close to 90°. In this respect, of possible significance is the separation between the palladium nuclei; its exceptionally short value of 2.6886(8) Å {*cf.* approx. 2.81 Å for the [(dippp)Pd]$_2$(μ-H)$_2$ series}[22] may represent an electrostatic interaction between the electron-rich Pd^0 centre and the cationic Pd^{II}, or, more likely a co-ordinate bond[35] from Pd(2) to cationic Pd(1). This bond is bridged by the CO group, which may be designated as semi-bridging[36] on the basis of its unequal span across the two non-equivalent palladium centres and the bent Pd(2)–C(29)–O(1) angle of 160.1(2)°. The P(2)–Pd(1)–C(30) angle of 177.7(2)° also seems to preclude an agostic interaction between Pd(2) and the methyl group; if such an agostic interaction were operating a more acute angle might be expected. Also of interest is the unusual disposition of the co-ordination planes: the plane defined by P(1)–Pd(1)–P(2) is tilted to that defined by P(3)–Pd(2)–P(4) by an angle of 92.10°, *i.e.* the co-ordination planes of the palladium nuclei are normal to each other; as discussed below, this structural feature complicated the solution behaviour.

Table 1 Crystallographic data for [(dippe)Pd(μ-CO)(dippe)PdMe]{B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$}·0.5C$_7$H$_8$*

Formula	$C_{62}H_{79}BF_{24}OP_4Pd_2\cdot 0.5C_7H_8$
M	1689.84
Colour, habit	Yellow, plate
Crystal size/mm	0.15 × 0.35 × 0.40
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	17.134(2)
b/Å	18.454(2)
c/Å	12.932(2)
α/°	93.22(1)
β/°	94.98(1)
γ/°	70.366(7)
U/Å^3	3835.1(8)
Z	2
ρ_{calc}/g cm^{-3}	1.463
F(000)	1714
μ(Mo-Kα)/cm^{-1}	6.49
Transmission factors	0.82–1.00
Scan type	ω–2θ
Scan range/° in ω	1.26 + 0.35 tan θ
Scan speed/° min^{-1}	16 (up to 8 rescans)
Data collected	$+h, \pm k, \pm l$
$2\theta_{max}$/°	50
Crystal decay (%)	22.5
Total reflections	13 984
Unique reflections	13 489
R_{merge}	0.054
Reflections with $I \geqslant 3\sigma(I)$	5769
No. of variables	927
R	0.044
R'	0.039
S	2.05
Max. Δ/σ (last cycle)	0.14
Residual density/e Å^{-3}	−0.51, +0.48

* T 294 K, Rigaku AFC6S diffractometer, Mo-Kα radiation (λ = 0.710 69 Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), $\sigma^2(F^2) = [S^2(C + 4B)]/\mathrm{Lp}^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\Sigma w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$ and $S = [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{\frac{1}{2}}$. Values given for R, R' and S are based on those reflections with $I \geqslant 3\sigma(I)$.

We have yet to reconcile the solid-state structure of **6** with that observed in solution, and in fact under ^{13}CO the species in solution is certainly not **6** but an allied dinuclear palladium complex to whose core two distinct carbonyl units are co-ordinated (*viz.* the ^{31}P-{^{1}H} NMR spectrum exhibits a doublet of doublets with two values of J_{PC} observed). Nevertheless, an analytically pure, crystalline sample of **6** dissolved in [^{2}H$_8$]THF does give a singlet at δ 58.6 in its ^{31}P-{^{1}H} NMR spectrum, and if ^{13}CO is introduced the doublet of doublet pattern is observed centred at δ 58.8. It appears that the ^{31}P-{^{1}H} NMR chemical shifts of the two species are more or less coincident, and that the species giving rise to the ABX pattern is the dicarbonyl, [Pd(dippe)(μ-^{13}CO)$_2$Pd(dippe)Me][BAr$_4$] **6a**[BAr$_4$], the carbonyl adduct of **6**;[37] the structure of the dicarbonyl is unknown, but must be similar to the isolated monocarbonyl **6** with the added proviso that the two bridging carbonyls are inequivalent. All attempts to isolate dicarbonyl **6a** simply result in isolation of **6** as the extra CO group is lost upon crystallization. It is worthwhile adding in passing that zerovalent palladium species such as Pd(dippp)CO (see below) and Pd(dippp)(CO)$_2$ have been characterized in solution, and the CO ligand is quite labile.[38] Admittedly, the low-field carbonyl absorptions in the ^{13}C-{^{1}H} NMR spectrum observed for **6a**, at δ 236.4 and 228.1, could be consistent with acyl carbons, but since both carbonyls bridge two palladium centres (as witnessed by their appearance as binomial quintets), the low-field chemical shifts are quite appropriate for bridging ligands.[39,40]

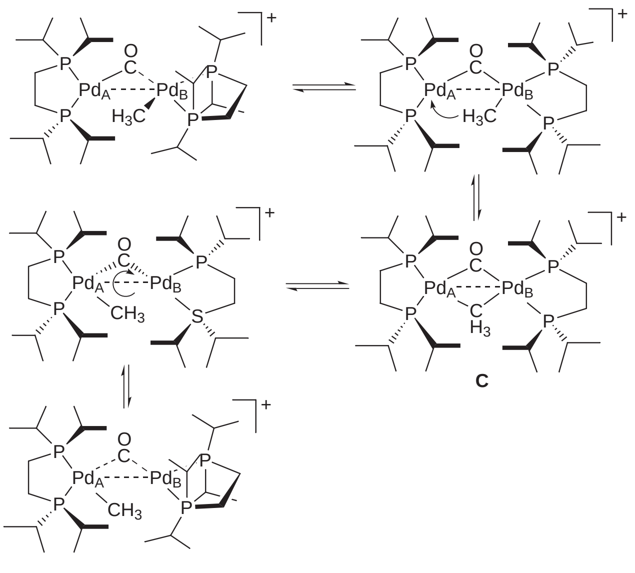
Table 2 Selected intramolecular bond distances (Å) and angles (°) observed in [Pd(dippe)(μ-CO)Pd(dippe)Me][BAr$_4$] **6**[BAr$_4$]

Pd(1)–Pd(2)	2.6886(8)	P(2)–C(5)	1.829(8)
Pd(1)–P(1)	2.302(2)	P(2)–C(6)	1.852(7)
Pd(1)–P(2)	2.332(2)	P(3)–C(15)	1.85(1)
Pd(1)–C(29)	2.32(1)	P(3)–C(17)	1.82(1)
Pd(1)–C(30)	2.172(7)	P(3)–C(18)	1.844(9)
Pd(2)–P(3)	2.325(2)	P(4)–C(16)	1.837(8)
Pd(2)–P(4)	2.340(2)	P(4)–C(19)	1.835(9)
Pd(2)–C(29)	1.87(1)	P(4)–C(20)	1.841(8)
P(1)–C(1)	1.831(7)	O(1)–C(29)	1.130(9)
P(1)–C(3)	1.822(8)	C(2)–C(2)	1.51(1)
P(1)–C(4)	1.84(1)	C(15)–C(16)	1.41(1)
P(2)–C(2)	1.849(7)		
Pd(2)–Pd(1)–P(1)	170.32(6)	Pd(1)–P(2)–C(2)	107.2(2)
Pd(2)–Pd(1)–P(2)	102.94(5)	Pd(1)–P(2)–C(5)	117.0(3)
Pd(2)–Pd(1)–C(29)	43.1(2)	Pd(1)–P(2)–C(6)	119.0(3)
Pd(2)–Pd(1)–C(30)	78.5(2)	C(2)–P(2)–C(5)	103.3(3)
P(1)–Pd(1)–P(2)	86.74(7)	C(2)–P(2)–C(6)	103.4(3)
P(1)–Pd(1)–C(29)	135.4(2)	C(5)–P(2)–C(6)	105.1(4)
P(1)–Pd(1)–C(30)	91.9(2)	Pd(2)–P(3)–C(15)	106.1(3)
P(2)–Pd(1)–C(29)	100.9(3)	Pd(2)–P(3)–C(17)	120.7(3)
P(2)–Pd(1)–C(30)	177.7(2)	Pd(2)–P(3)–C(18)	114.6(3)
C(29)–Pd(1)–C(30)	81.4(3)	C(15)–P(3)–C(17)	105.4(6)
Pd(1)–Pd(2)–P(3)	170.32(6)	C(15)–P(3)–C(18)	104.4(5)
Pd(1)–Pd(2)–P(4)	102.94(5)	C(15)–P(3)–C(18)	104.1(5)
Pd(1)–Pd(2)–C(29)	43.1(2)	Pd(2)–P(4)–C(16)	105.9(3)
P(3)–Pd(2)–P(4)	86.74(7)	Pd(2)–P(4)–C(19)	120.4(3)
P(3)–Pd(2)–C(29)	135.4(2)	Pd(2)–P(4)–C(20)	118.5(3)
P(4)–Pd(2)–C(29)	100.9(3)	C(16)–P(4)–C(19)	104.3(4)
Pd(1)–P(1)–C(1)	106.6(3)	C(16)–P(4)–C(20)	102.7(4)
Pd(1)–P(1)–C(3)	114.7(3)	C(16)–P(4)–C(20)	102.8(4)
Pd(1)–P(1)–C(4)	120.0(3)	Pd(1)–C(29)–Pd(2)	79.0(4)
C(1)–P(1)–C(3)	103.7(4)	Pd(1)–C(29)–O(1)	120.8(8)
C(1)–P(1)–C(4)	106.7(5)	Pd(2)–C(29)–O(1)	160.1(2)
C(3)–P(1)–C(4)	103.7(5)		

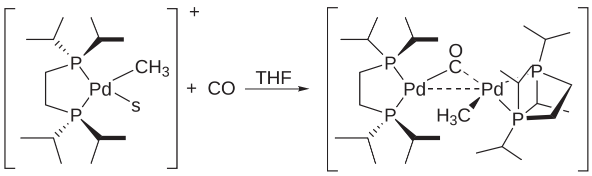
As regards the apparent equivalence of the phosphorus nuclei in the ^{31}P-{^{1}H} NMR spectrum, clearly an exchange process must be operating which serves to equate the phosphorus nuclei. Such a process must not only interchange the phosphorus nuclei on each one of the dippe ligands, it must also equate the donor nuclei on alternate ligands. Lability of the CO group would partially satisfy the first requirement, however since **6** is a 30-e dinuclear species, it is likely that the CO remains tightly bound to the metal core. Alternatively, the equivalence of the phosphorus donors may be explained by an intermediate with both a bridging methyl and a bridging carbonyl group, and with the co-ordination planes coplanar. Transfer of the methyl or carbonyl group may occur in either a stepwise or concerted fashion, and rapid equilibration results in the observation of a singlet in the ^{31}P-{^{1}H} NMR spectrum. A proposal for this fluxional process is shown in Scheme 1. We suggest that one end of the dinuclear unit rotates to generate two coplanar units which then undergo a symmetrization process through a species such as **C** with equivalent palladium nuclei; such a rearrangement allows for methyl group and CO transfer between the two palladium centres and exchange of the phosphorus donors by virtue of the sense of the rotation to form **C**.

At low temperature (<−70 °C), the singlet at δ 58.6 splits into four broad signals, *i.e.* four phosphorus environments, and is therefore consistent with the solid-state structure. Such fluxionality was also observed in the related cation, {[(dippp)Pd]$_2$-(μ-H)(μ-CO)}$^+$,[39,40] but in this case the limiting spectrum was not reached.

Mechanistic experiments



Scheme 1



(6)

2 (s = THF)

6

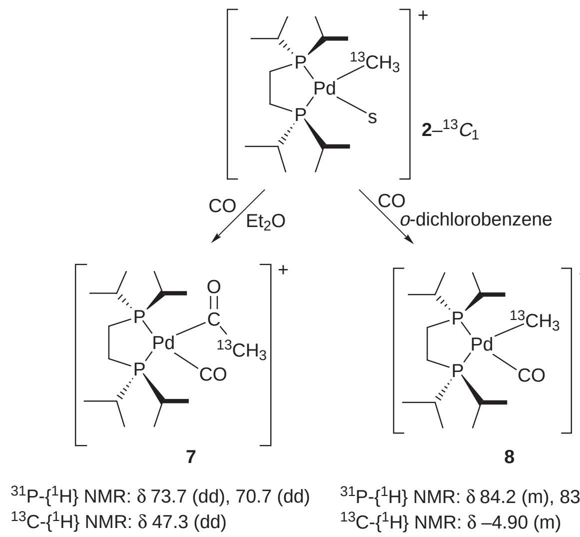
^{31}P-{^{1}H} NMR: δ 58.6 (s)
IR ν$_{CO}$ (KBr disc): 1830 cm^{-1}

The mechanism of formation of dinuclear **6** from the mononuclear methyl cation **2** and CO is not obvious. As shown as a reminder in equation (6), the initial reactants were [Pd(dippe)-Me(s)]$^+$ **2**, formally a Pd^{II} species, and carbon monoxide in THF. The product isolated is a Pd^{II}/Pd^0 dimer. Thus, somewhere along the reaction pathway a divalent palladium nucleus undergoes a formal two-electron reduction to Pd^0.

When the CO reaction was performed in Et$_2$O–C$_6$D$_6$ with **2**-$^{13}C_1$, the ^{31}P-{^{1}H} NMR spectrum revealed two sets of doublet of doublets at δ 73.7 and 70.7 ($J_{PP'}$ = 40.6 Hz), and in the ^{13}C-{^{1}H} NMR spectrum a doublet of doublets at δ 47.3 was observed (J_{CP} = 38.7, $J_{CP'}$ = 17.3 Hz). This species is formulated as the square-planar, acyl–carbonyl complex, [Pd(dippe)-(CO^{13}CH$_3$)CO]$^+$ **7** with the two phosphorus–carbon coupling constants of the $^3J_{CP}$ type corresponding to a *trans* and *cis* coupling respectively. When the reaction of **2**-$^{13}C_1$ was performed in the poorly co-ordinating solvent *o*-dichlorobenzene under a *deficiency* of CO, the carbonyl adduct of the labelled methyl cation, [Pd(dippe)(^{13}CH$_3$)CO]$^+$ **8**, was observed (Scheme 2), as indicated by a new ABX pattern in the ^{31}P-{^{1}H} NMR at δ 84.2 and 83.8 ($J_{PP'}$ = 21.2 Hz), and the corresponding spectrum in the ^{13}C-{^{1}H} NMR centred at δ −4.9 [J_{CP} (*trans*) = 105, $J_{CP'}$ (*cis*) = −8.5 Hz], whose upfield value indicates a Pd–Me group rather than a Pd–acyl.[41] These results are summarized in Scheme 2.

From these latter experiments one can obtain spectroscopic parameters for acyl–carbonyl **7** and methyl–carbonyl **8** to use in subsequent experiments described below; the change in solvents shown in Scheme 2 provided the best conditions to prepare the putative intermediates **7** and **8**.

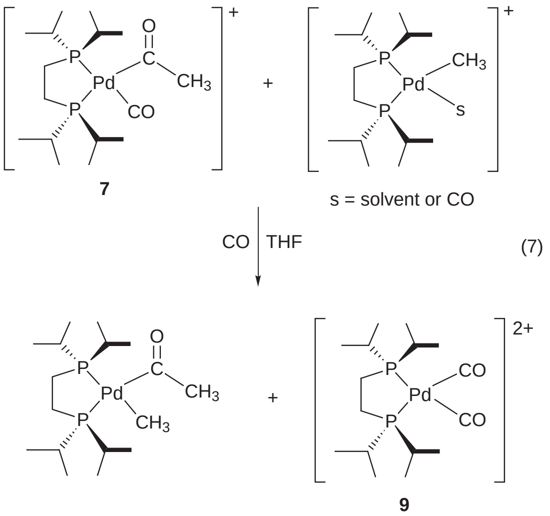
As mentioned above, at moderate pressures of CO (1–4 atm), signals due to a putative Pd–acyl species were conspicuously absent from a solution of **2** in [^{2}H$_8$]THF. However, when an NMR sample of the labelled precursor **2**-$^{13}C_1$ was prepared under lower pressures of CO (300 mmHg pressure), signals attributable to both [Pd(dippe)(CO^{13}CH$_3$)CO]$^+$ **7** and [Pd-(dippe)(^{13}CH$_3$)CO]$^+$ **8** could be observed in the ^{31}P-{^{1}H} NMR spectrum, which diminished in intensity relative to the peak due to **6** on standing. Also a peak at δ 81.0 was observed that grows

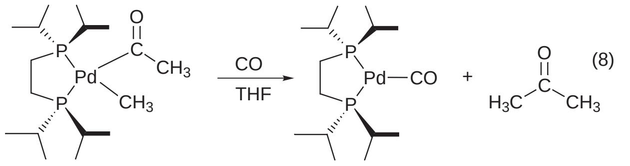


Scheme 2

in with the peak at δ 58.7 but then diminishes in intensity on standing with several new absorptions above δ 100 observed. The observation of **7** and **8** seems to indicate that these species are intermediates in the formation of **6**/**6a**, and not the converse.

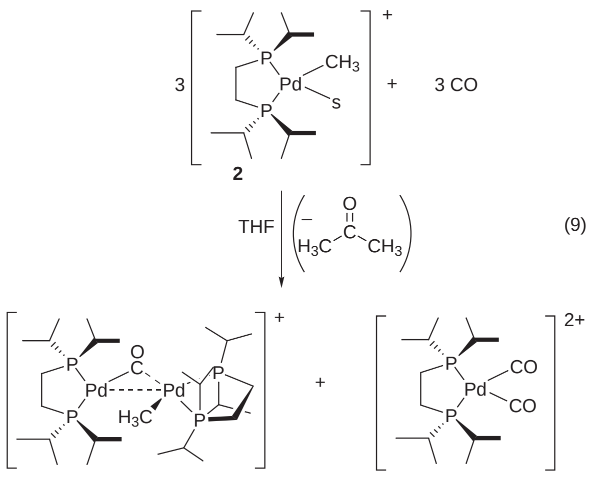
When the volatiles were distilled away from an NMR sample of **6** prepared using ^{13}CO, a peak at δ 204.0 was observed in the ^{13}C-{^{1}H} NMR spectrum of the distillate, and a doublet resonance was observed at δ 2.03 ($J_{HC} = 6.0$ Hz) in the ^{1}H NMR spectrum, *i.e.* chemical shifts consistent with *acetone*.[42,43] The identity of this coproduct was confirmed by GC-MS, which, along with peaks for Et₂O and [$^2H_8$]THF, gave a molecular ion at *m*/*z* 59, *i.e.* corresponding to $H_3C(^{13}CO)CH_3$. For the experiment performed with **2**-$^{13}C_1$ under ^{12}CO, $H_3{}^{13}C(CO)$-$^{13}CH_3$ was identified by GC-MS. The origin of acetone is thus due to the methyl group of the starting material **2**. In order to account for the coupling of two methyl units and the one carbonyl we must invoke hydrocarbyl transfer, presumably between **7** and **8** or **2**, of a methyl group to a palladium acyl species (or conversely, an acyl group to a palladium methyl species), of the kind represented in equation (7). Under CO, such a process would produce two new compounds: a *neutral* Pd^{II} complex, Pd(dippe)(COMe)Me, which reductively eliminates to give acetone and a zerovalent palladium species, presumably Pd(dippe)CO [equation (8)]; and a Pd^{II} species, [Pd(dippe)]$^{2+}$ or one of its carbonyl adducts. It is this dicationic species that therefore gives rise to the peak at δ 81.9 in the ^{31}P-{^{1}H} NMR spectrum. The identity of this species is probably [Pd(dippe)(CO)$_2$](BAr$_4$)$_2$ **9** since under ^{13}CO, the peak at δ 81.0 appears as a second-order multiplet due to the [AX]$_2$ spin system of the square-planar [Pd(dippe)(^{13}CO)$_2$]$^{2+}$ dication. In a separate experiment we tried to access these Pd^{2+} complexes by the addition of 2 equivalents of HBAr$_4$ to a solution of Pd(dippe)Me$_2$ in THF. The evolution of a gas was indeed observed, but unfortunately the species so produced, presumably [Pd(dippe)(THF)$_2$][BAr$_4$]$_2$ **10b**[BAr$_4$]$_2$, rapidly polymerizes the THF solvent which makes characterization impossible. In CD$_3$CN spectroscopic parameters for the dication [Pd(dippe)(N≡CCD$_3$)$_2$][BAr$_4$]$_2$ **10a**[BAr$_4$]$_2$ can be obtained and its ^{31}P-{^{1}H} NMR spectrum exhibits a singlet at δ 118.9. However, CO is too poorly co-ordinating to displace the strongly bound acetonitrile molecules from the palladium centre, and **9** was therefore inaccessible by this route. However, when Pd(dippe)Me$_2$ is treated with 2 equivalents of HBAr$_4$ in THF, but under stringent temperature control (*i.e.* a temperature of −78 °C was not exceeded) evidence for **9** could be obtained. Thus, after the reaction mixture was warmed to −20 °C and the volatiles were removed, a solution of the residue in CD$_2$Cl$_2$ under ^{12}CO exhibited a singlet at δ 83.8 in the ^{31}P-{^{1}H} NMR spectrum. When the solution was warmed to room temperature, the singlet at δ 83.8 diminished in intensity and a new singlet was observed at δ 115.6. From the original mixture, crystals of the bis(THF) dication **10b** were indeed isolated, after recrystallization from methylene chloride at low temperature (<−20 °C). In CD$_2$Cl$_2$ **10a** briefly gives a singlet in the ^{31}P-{^{1}H} NMR spectrum at δ 118.9, to be replaced by a singlet due to the decomposition product at δ 115.6. Thus, one can conclude that the singlet at δ 81.9 in the original reaction between **2** and CO was in fact [Pd(dippe)(CO)$_2$]$^{2+}$. The slight discrepancy in chemical shift may be explained by the different NMR solvent used in each case. To summarize, the mononuclear acyl **7** combines with a Pd–Me complex, whose methyl group is exchanged for the carbonyl of **7** (possibly *via* the intermediacy of a dinuclear intermediate). The complex Pd(dippe)(COMe)Me is thereby formed, which, in the presence of CO, reductively eliminates acetone to generate the zerovalent palladium complex, Pd(dippe)CO [equations (7) and (8)]. Meanwhile, the other product arising from the reaction of **7** and **8**, the dication [Pd(dippe)(CO)$_2$]$^{2+}$ **9**, eventually decomposes by reacting with the solvent. This decomposition side reaction does not complicate isolation of the dinuclear final product **6**.





The extrusion of acetone thus produces one of the elements required for formation of **6**/**6a**, the zerovalent Pd(dippe)CO unit. It is proposed that this electron-rich moiety acts as a donor towards [Pd(dippe)Me]$^+$ **2**, which is present in the mixture, in a type of Lewis acid–metal base interaction. Therefore we can finally balance the reaction of CO and **2** to give **6** as shown in equation (9).

As further confirmation of the mixed-valence nature of dinuclear **6**, we prepared an analogue using independently prepared Pd(dippp)CO, and authentic [Pd(dippe)Me(OEt$_2$)]$^+$ **2**. The use of the three-carbon backbone ligand dippp for the starting Pd^0 portion represents a negligible chemical change, but a dramatic change in magnetic resonance results, and this provides excellent handles for ^{31}P-{^{1}H} NMR spectroscopy. As shown in equation (10), if Pd(dippp)CO is generated *in situ* {*i.e.* by placing a THF solution of [Pd(dippp)]$_2$ under CO}, and 1 equivalent of [Pd(dippe)Me(OEt$_2$)]$^+$ **2** is added, a pair of triplets are observed in the ^{31}P-{^{1}H} NMR spectrum of the solution at δ 53.8 and 23.8 ($J_{PP'} = 28.5$ Hz). This result is precisely



2

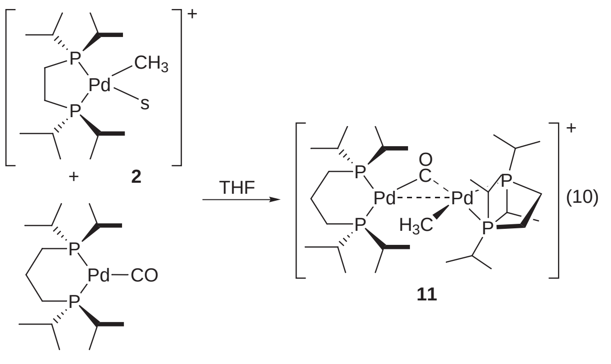
(9)

6

9

what is expected if adduct formation between Pd(dippp)CO and **2** occurs, and the formation of {[Pd(dippp)(μ-CO)Pd(dippe)-Me]} **11**, the dippp analogue of **6**, is indicated.

It should be noted that only one of the two limiting, instantaneous structures of **11** is shown in equation (10); as before, an exchange process serves to equilibrate the phosphorus nuclei of each ligand (*cf.* Scheme 1).



2

(10)

11

Conclusion

From this work, one major conclusion emerges and that is that *dinuclearity* figures prominently in these cationic palladium methyl complexes stabilized with electron-rich diphosphine ligands. It is useful to review the occurrences of dinuclear systems in this study. The reaction of the methyl cation **2** with H_2 generates a *dinuclear* palladium hydride species; the interchange of alkyl groups between neutral dialkyl derivatives and cationic alkyl complexes is proposed to involve a *dinuclear* intermediate; and the formation of a *dinuclear* mixed-valence complex is observed upon carbonylation of the methyl cation **2** in THF. This is hardly coincidence but not easily rationalized. If one examines the literature on Pd chemistry, dinuclearity is not particularly common;[15] it would appear that electron-rich diphosphine ancillary ligands tend to promote this kind of behaviour. Nitrogen-based ligands such as diimines, bipyridine or phenanthroline apparently do not promote formation of dinuclear Pd complexes; nevertheless, it should be emphasized that beyond these observations we have no explanation.

The copolymerization of carbon monoxide with olefins is typically carried out in MeOH or CH_2Cl_2.[4,5,8,11,16,32] To our knowledge no one has reported the use of THF for this reaction although there is one brief report[44] that mentions that no polymerization was observed in THF. It stands to reason that any strongly co-ordinating solvent will compete for substrate binding (*i.e.* co-ordination of ethylene or carbon monoxide) and reduce the tendency for the propagation step. However, from this work, we have shown that there is a further point to consider and that is the formation of catalytically inactive species due to the presence of strongly co-ordinating solvents such as THF. In the case reported here, catalyst poisoning occurs by formation of an inactive dinuclear complex.

In this report we have described some reactivity patterns for $[Pd(dippe)Me(s)]^+$ **2**. The fact that this cationic system shows enhanced reactivity towards small molecules as compared to the inertness of its parent complex, $Pd(dippe)Me_2$, is apparent from its reaction with dihydrogen. Late metals can activate small molecules by oxidative addition pathways, and the reaction of **2** to give $\{[Pd(dippe)]_2(\mu\text{-}H)_2\}^+$ **4** could be accounted for by an oxidative addition of **2** to give a Pd^{IV} species, followed by a reductive elimination of methane to give **4**. Such a mechanism is in marked contrast to the inability of both neutral Pd^{II} and Pd^0 to add dihydrogen.[45] The rapid reaction of **2** with H_2 could even be said to resemble hydrogenolysis (*i.e.* σ-bond metathesis[46]), a process that is normally associated with the alkyls of the early transition metals. This apparent reversal of the normal trends of reactivity of the Periodic Table has been noted in a similar system, *viz.* $\{Cp^*Ir(PMe_3)Me(CH_2Cl_2)\}BAr_4$,[47,48] a cationic complex of Ir^{III} which will induce selective C–H activation in alkanes.

Experimental

The GC-MS analysis was performed by the Mass Spectrometry Service of the University of British Columbia upon a KRATOS MS80 RFA instrument. Other procedures are identical to that reported previously.[22,23]

The salt $HBAr_4$ was prepared by a literature method,[7] as was $B(C_6F_5)_3$.[49] Methyllithium (Aldrich, halide content <0.05 mol L^{-1}) was used as supplied as a 1.4 mol L^{-1} solution in Et_2O; $PhCH_2MgCl$ (Aldrich) was used as supplied as a 1.0 mol L^{-1} solution in Et_2O; $Mg(^{13}CH_3)_2$ was prepared by a literature method and used as either a 0.05 mol L^{-1} solution in Et_2O, or recrystallized from benzene–pentane as $Mg(^{13}CH_3)_2\cdot diox$ (diox = 1,4-dioxane).[50] The metal precursor Pd(COD)MeCl was prepared according to the literature,[51] as were $Pd(dippe)Cl_2$ and $Pd(dippp)I_2$.[22,23] Methylene chloride was distilled from CaH_2 under N_2. Acetonitrile was dried over activated 4 Å molecular sieves, distilled from trap to trap, and stored over molecular sieves. The solvents CD_2Cl_2 and CD_3CN were distilled from CaH_2 after a prolonged period at reflux under N_2; $[^2H_8]$THF was distilled from sodium benzophenone under N_2; $C_6D_4Cl_2$-*o* was distilled from CaH_2 under N_2. All deuteriated solvents were subjected to four freeze–pump–thaw cycles.

Preparations

$Pd(dippe)Me_2$. To a slurry of $Pd(dippe)Cl_2$ (1.54 g; 3.50 mmol) in THF (30 mL) at −78 °C was added a solution of MeLi (5.0 mL; 7.0 mmol) dropwise over 5 min. The cooling bath was then removed, and as the mixture attained room temperature a reaction ensued evidenced by the disappearance of the $Pd(dippe)Cl_2$ and the formation of a clear, dark brown solution. The solution was stirred for 1 h after which time the solvent was removed *in vacuo*. The brown residue was extracted with toluene (25 mL), passed through a frit lined with Celite to remove LiCl, and concentrated to a small volume (*ca.* 3 mL). The brown solution was layered with pentane (10 mL) and cooled to −40 °C to give colourless crystals of $Pd(dippe)Me_2$ after 12 h (1.25 g; 89% yield). ^1H NMR ($[^2H_8]$toluene, 500.13 MHz): δ 1.88 (spt, 4 H, C*H*MeMe′, $J_{HMe} = 7.1$), 1.14 (m, 4 H, PCH_2CH_2P), 1.06 (dd, 12 H, CH*Me*Me′, $J_{HMe} = 7.1$, $J_{MeP} = 15.4$), 0.84 (dd, 12 H, CHMe*Me′*, $J_{HMe} = 7.1$, $J_{MeP} = 12.4$), 0.72 [dd, 6 H, PdMe_2, J_{MeP} (*trans*) = 6.6, J_{MeP} (*cis*) = 1.0 Hz]. $^{31}P\text{-}\{^1H\}$ NMR ($[^2H_8]$toluene): δ 61.0 (Found: C, 47.69; H, 9.42. Calc. for $C_{16}H_{38}P_2Pd$: C, 48.19; H, 9.60%).

Following the preparation of $Pd(dippe)Me_2$, Pd(dippe)-

$(^{13}CH_3)_2$ was similarly prepared, with Pd(dippe)Cl$_2$ (0.509 g; 1.16 × 10^{-3} mol) and Mg(^{13}CH$_3$)$_2$(C$_4$H$_8$O)$_2$ (0.165 g; 1.16 × 10^{-3} mol). Recrystallization from toluene (1 mL) layered with hexanes gave colourless crystals (0.371 g; 80% yield). ^{1}H NMR (C$_6$D$_6$, 500.13 MHz): δ 1.88 (spt, 4 H, C*H*MeMe′, J_{HMe} = 7.1), 1.14 (m, 4 H, PC*H*$_2$C*H*$_2$P), 1.09 (dd, 12 H, CH*Me*Me′, J_{HMe} = 7.1, J_{MeP} = 15.4), 0.83 (dd, 12 H, CHMe*Me*′, J_{HMe} = 7.1, J_{MeP} = 12.4), 0.87 [ddd, 6 H, Pd**Me*$_2$, J_{HC} = 124.0, J_{MeP} (*trans*) = 6.6, J_{MeP} (*cis*) = 1.0 Hz]. ^{31}P-{^{1}H} (C$_6$D$_6$, 81.015 MHz): δ 65.4 [m, J_{PC} (*trans*) = 108.5, J_{PC} (*cis*) = −10.5, $J_{PP'}$ = 8.1 Hz]. ^{13}C-{^{1}H} (C$_6$D$_6$, 50.32 MHz): δ 0.0 [m, J_{CP} (*trans*) = 108.5, J_{CP} (*cis*) = −10.5, $J_{CC'}$ = 0.5 Hz]. Microanalysis was not obtained.

Pd(dippp)Me$_2$. The complex Pd(dippp)Me$_2$ was synthesized as for Pd(dippe)Me$_2$, with Pd(dippp)I$_2$ (0.565 g; 8.88 × 10^{-4} mol) and MeLi (1.3 mL; 1.80 × 10^{-3} mol). Successive recrystallizations from toluene (3 mL) layered with hexanes (6 mL) gave Pd(dippp)Me$_2$ as colourless crystals (0.179 g; 49% yield). ^{1}H NMR (C$_6$D$_6$, 299.99 MHz): δ 2.45 (m, 2 H, PCH$_2$C*H*$_2$CH$_2$P), 1.92 (m, 4 H, C*H*MeMe′, J_{HMe} = 7.2), 1.58 (m, 4 H, PC*H*$_2$CH$_2$C*H*$_2$P), 1.14 and 0.91 (dd, 24 H, CHMe*Me*′, J_{MeH} = 7.2, J_{MeP} = 15.0), 0.59 [dd, 6 H, Pd*Me*$_2$, J_{MeP} (*trans*) = 5.0, J_{MeP} (*cis*) = 1.0 Hz]. ^{31}P-{^{1}H} NMR (C$_6$D$_6$, 121.41 MHz): δ 16.4 (Found: C, 49.15; H, 9.95. Calc. for C$_{17}$H$_{40}$P$_2$Pd: C, 49.46; H, 9.77%).

Pd(dippe)(CH$_2$Ph)$_2$. As for Pd(dippe)Me$_2$ with Pd(dippe)Cl$_2$ (1.09 g; 2.48 × 10^{-3} mol) and PhCH$_2$MgCl (5 mL; 5.0 × 10^{-3} mol). Recrystallization from toluene (2 mL) layered with hexanes (10 mL) afforded Pd(dippe)(CH$_2$Ph)$_2$ as clear brown needles (1.00 g; 73% yield). ^{1}H NMR (C$_6$D$_6$, 500.13 MHz): δ 7.43 (m, 4 H, *o*-H of Ph), 7.21 (m, 4 H, *m*-H of Ph), 6.96 (m, 2 H, *p*-H of Ph), 3.11 (dd, 4 H, C*H*$_2$Ph, J_{HP} = 9.0, $J_{HP'}$ = 7.5), 1.75 (spt, 4 H, C*H*MeMe′, J_{HMe} = 7.0), 1.00 (m, 4 H, PC*H*$_2$C*H*$_2$P), 0.91 and 0.82 (dd, 24 H, CH*MeMe*′, J_{MeP} = 16.0, J_{MeH} = 7.0 Hz). ^{31}P-{^{1}H} NMR (C$_6$D$_6$, 202.47 MHz): δ 62.0 (Found: C, 60.75; H, 7.94. Calc. for C$_{28}$H$_{46}$P$_2$Pd: C, 61.03; H, 8.01%).

[Pd(dippe)(η^3-CH$_2$Ph)]{B(C$_6$F$_5$)$_3$CH$_2$Ph}. To a solution of Pd(dippe)(CH$_2$Ph)$_2$ (0.100 g; 1.82 × 10^{-4} mol) in Et$_2$O (2 mL) was added solid B(C$_6$F$_5$)$_3$ (0.093 g; 1.82 × 10^{-4} mol) with stirring. The initial brown colour discharged to give a colourless solution. The solvent was removed *in vacuo* to give a slimy brown oil which resisted crystallization. The product was characterized in solution. ^{1}H NMR (CD$_3$CN, 200.12 MHz): δ 7.75, 7.70, 7.58, 7.10 and 6.59 (m, 10 H, CH$_2$*Ph* and BCH$_2$*Ph*), 3.09 (d, 2 H, C*H*$_2$Ph, J_{HP} = 9.4 Hz), 2.54 (s, 2 H, PhC*H*$_2$B), 2.40 and 2.10 (m, 4 H, C*H*MeMe′), 2.04 and 1.81 (m, 4 H, PC*H*$_2$C*H*$_2$′P), 1.17, 1.06, 0.95 and 0.92 (m, 24 H, CH*MeMe*′). ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$, 121.42 MHz): δ 89.3 (d, 1 P, $J_{PP'}$ = 30.6), 76.9 (d, 1 P, $J_{PP'}$ = 30.6 Hz).

[Pd(dippe)(η^3-CH$_2$C$_6$H$_5$)][BAr$_4$] 1[BAr$_4$]. To a solution of Pd(dippe)(CH$_2$Ph$_2$)$_2$ (0.072 g; 1.28 × 10^{-4} mol) in THF (10 mL) at −10 °C was added a solution of HBAr$_4$ (0.130 g; 1.28 × 10^{-4} mol) in THF (1 mL). The original dark colour became clear. After the solvent was removed, the residue was dissolved in Et$_2$O (2.5 mL), and the solution placed in the freezer. Colourless crystals appeared after 24 h (0.127 g; 76%). ^{1}H NMR (CD$_2$Cl$_2$, 500.13 MHz): δ 7.75 (br s, 8 H, *o*-H of Ar$_4$), 7.68 (m, 1 H, *p*-H of η^3-CH$_2$Ph), 7.55 (br s, 4 H, *p*-H of Ar$_4$), 7.30 (m, 2 H, *m*-H of η^3-CH$_2$Ph), 6.41 (m, 2 H, *o*-H of η^3-CH$_2$Ph), 3.06 (d, 2 H, η^3-C*H*$_2$Ph, J_{HP} = 7.8), 2.37 and 1.98 (dspt, 4 H, C*H*MeMe′, J_{HP} = 1.8, J_{HMe} = 7.2), 2.04 and 1.76 (dt, 4 H, PC*H*$_2$C*H*$_2$′P, J_{HP} = 19.7, $J_{HH'}$ = 7.0), 1.07, 1.10, 0.92 and 0.75 (dd, 24 H, CH*MeMe*′, J_{MeP} = 14.7, J_{MeH} = 7.2 Hz). ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$, 121.42 MHz): δ 88.7 (d, 1 P, $J_{PP'}$ = 32.1), 75.2 (d, 1 P, $J_{PP'}$ = 32.1 Hz) (Found: C, 48.16; H, 3.96. Calc. for C$_{53}$H$_{51}$BF$_{24}$P$_2$Pd: C, 48.11; H, 3.89%).

[Pd(dippe)(s)Me][BAr$_4$] 2[BAr$_4$]. To a solution of Pd(dippe)Me$_2$ (0.126 g; 3.16 × 10^{-4} mol) in Et$_2$O (5 mL) was added a solution of HBAr$_4$ (0.320 g; 3.16 × 10^{-4} mol) in Et$_2$O (5 mL) at −10 °C. The solution vigorously effervesced and lightened in intensity. The volatiles were removed *in vacuo* and the residue was recrystallized from Et$_2$O (3 mL) and placed in the freezer. Colourless crystals appeared after 24 h (0.323 g; 82% yield). ^{1}H NMR ([^{2}H$_8$]THF, 500.13 MHz): δ 7.79 (br s, 8 H, *o*-H of Ar$_4$), 7.58 (br s, 4 H, *p*-H of Ar$_4$), 3.35 (q, 4 H, free OC*H*$_2$CH$_3$, $J_{HH'}$ = 7.0), 2.43 and 2.31 (spt, 4 H, C*H*MeMe′, J_{HMe} = 7.2), 2.15 and 2.11 (dt, 4 H, PC*H*$_2$C*H*′$_2$P, J_{HP} = 13.3, $J_{HH'}$ = 6.1), 1.31, 1.26, 1.24 and 1.21 (dd, 24 H, CH*MeMe*′, J_{MeP} = 16.0, J_{MeH} = 7.2), 1.07 (t, 6 H, free OCH$_2$C*H*$_3$, $J_{HH'}$ = 7.0), 0.63 [dd, 3 H, Pd–*Me*, J_{MeP} (*trans*) = 6.3, J_{MeP} (*cis*) = 0.9 Hz]. ^{31}P-{^{1}H} NMR ([^{2}H$_8$]THF, 202.42 MHz): δ 86.0 (d, 1 P, $J_{PP'}$ = 17.0), 69.0 (d, 1 P, $J_{PP'}$ = 17.0 Hz) (Found: C, 45.37; H, 4.00. Calc. for C$_{47}$H$_{47}$BF$_{24}$P$_2$Pd: C, 45.27; H, 3.80%).

Labelled **2**-^{13}*C*$_1$ was prepared likewise from Pd(dippe)(^{13}CH$_3$)$_2$ and HBAr$_4$. ^{31}P-{^{1}H} NMR (C$_6$D$_6$–Et$_2$O, 81.015 MHz): δ 87.9 [dd, 1 P, $J_{PP'}$ = 16.7, J_{PC} (*cis*) = 2.8], 67.3 [dd, 1 P, $J_{P'P}$ = 16.7, J_{PC} (*trans*) = 86.1 Hz]. ^{13}C-{^{1}H} NMR (C$_6$D$_6$–Et$_2$O, 50.32 MHz): δ 4.49 [dd, J_{CP} (*trans*) = 86.1, J_{CP} (*cis*) = 2.8 Hz].

[Pd(dippp)(s)Me][BAr$_4$] 3[BAr$_4$]. As for **2** with Pd(dippp)Me$_2$ (0.086 g; 2.08 × 10^{-4} mol) and HBAr$_4$ (0.211 g; 2.08 × 10^{-4} mol). Recrystallization from Et$_2$O (2 mL) gave clear crystals which darkened on standing (0.100 g; 38% yield). ^{1}H NMR (CD$_2$Cl$_2$, 200.13 MHz): δ 7.63 (br s, 8 H, *m*-H of Ar$_4$), 7.50 (br s, 4 H, *p*-H of Ar$_4$), 3.67 (q, 4 H, OC*H*$_2$CH$_3$, $J_{HH'}$ = 7.0), 2.39 (m, 2 H, PCH$_2$C*H*$_2$CH′$_2$P), 2.10 (m, 4 H, C*H*MeMe′), 1.59 and 1.43 (m, 4 H, PC*H*$_2$CH$_2$C*H*′$_2$P), 1.15 (t, 6 H, OCH$_2$C*H*$_3$, $J_{HH'}$ = 7.0), 1.10 (m, 24 H, CH*MeMe*′), 0.60 [dd, 3 H, Pd–Me, J_{MeP} (*trans*) = 5.0, J_{MeP} (*cis*) = 1.0 Hz]. ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$, 81.015 MHz): δ 49.6 (d, 1 P, $J_{PP'}$ = 39.2), 16.2 (d, 1 P, $J_{PP'}$ = 39.2 Hz) (Found: C, 46.01; H, 3.59. Calc. for C$_{48}$H$_{49}$BF$_{24}$P$_2$Pd: C, 45.72; H, 3.92%).

{[Pd(dippe)]$_2$(μ-H)$_2$}[BAr$_4$]$_2$ 4[BAr$_4$]. Complex cation **2** (0.250 g; 1.89 × 10^{-4} mol) was dissolved in THF (10 mL), and the solution was subjected to four freeze–pump–thaw cycles. The solution was cooled to −196 °C and placed under 4 atm of dihydrogen. Upon warming to −78 °C the solution developed a deep red colour. The solution was warmed with stirring to 0 °C and the THF was removed *in vacuo*. The red residue remaining was dissolved in THF (2 mL) and cooled to −40 °C. Deep red needles deposited after 12 h (0.120 g; 51%). ^{1}H NMR ([^{2}H$_8$]THF, 500.13 MHz): δ 7.79 (br s, 16 H, *o*-H of Ar$_4$), 7.56 (br s, 8 H, *p*-H of Ar$_4$), 2.20 (spt, 8 H, C*H*MeMe′, J_{HMe} = 7.0), 2.08 (m, 8 H, PC*H*$_2$C*H*′$_2$P), 1.20 and 1.14 (dd, 48 H, CH*MeMe*′, J_{MeP} = 16.5, J_{MeH} = 7.0), −5.75 [qnt, 2 H, (μ-H)$_2$, J_{PH} = 55.0 Hz]. ^{31}P-{^{1}H} NMR ([^{2}H$_8$]THF, 202.42 MHz): δ 92.0 (Found: C, 45.01; H, 3.71. Calc. for C$_{92}$H$_{90}$B$_2$F$_{48}$P$_4$Pd$_2$: C, 44.81; H, 3.68%).

Methyl transfer between cation 2 and Pd(dippe)(^{13}CH$_3$)$_2$. To a solution of **2** (0.035 g; 2.81 × 10^{-5} mol) in Et$_2$O (0.20 mL) was added a solution of Pd(dippe)(^{13}CH$_3$)$_2$ (0.12 g; 2.82 × 10^{-5} mol) in C$_6$D$_6$ (0.20 mL). The products were characterized in solution. ^{31}P-{^{1}H} NMR (C$_6$D$_6$–Et$_2$O, 81.015 MHz): δ 71.0 (br s). ^{13}C-{^{1}H} NMR (C$_6$D$_6$–Et$_2$O, 50.32 MHz): δ −3.8 (br s).

Pd(dippe)(Me)CH$_2$Ph 5. To a solution of Pd(COD)MeCl (0.344 g; 1.26 × 10^{-3} mol) in THF (20 mL) was added a solution of dippe (0.330 g; 1.26 × 10^{-3} mol) in toluene (2 mL) to produce a white precipitate. The reaction vessel was then cooled to −78 °C in a dry-ice–acetone bath and a solution of KCH$_2$Ph (0.166 g; 1.26 × 10^{-3} mol) in THF (5 mL) was added by cannulation. The reaction mixture was allowed to warm to room temperature with stirring, and the solvent was removed *in vacuo* to give an orange residue. The residue was taken up in toluene

(20 mL), and this solution was passed through Celite. The filtrate was concentrated to 2 mL and then layered with hexanes (5 mL). After 24 h at −40 °C orange crystals deposited (0.453 g; 76% yield). ^1H NMR (C_6D_6, 500.13 MHz): δ 7.51 (m, 2 H, *m*-H of Ph), 7.26 (m, 2 H, *o*-H of Ph), 6.96 (m, 1 H, *p*-H of Ph), 3.18 [dd, 2 H, CH_2Ph, J_{HP} (*trans*) = 10.0, J_{HP} (*cis*) = 8.0], 1.81 and 1.83 (spt, 4 H, C*H*MeMe′, J_{HMe} = 7.5), 1.06 and 1.04 (m, 4 H, $PCH_2CH_2'P$), 1.00, 0.96, 0.82 and 0.75 (dd, 24 H, CH*MeMe*′, J_{HP} = 12.0, J_{MeH} = 7.5), 0.67 [dd, 3 H, Pd–Me, J_{MeP} (*trans*) = 7.0, J_{MeP} (*cis*) = 6.0 Hz]. ^{31}P-{^1H} NMR (C_6D_6, 202.42 MHz): δ 68.6 (d, 1 P, $J_{PP'}$ = 10.0), 60.4 (d, 1 P, $J_{PP'}$ = 10.0 Hz) (Found: C, 55.62; H, 8.88. Calc. for $C_{22}H_{42}P_2Pd$: C, 55.64; H, 8.91%).

[Pd(dippe)(μ-CO)Pd(dippe)Me][BAr$_4$] 6[BAr$_4$] and [Pd(dippe)(μ-^{13}CO)$_2$Pd(dippe)Me][BAr$_4$] 6a[BAr$_4$]. In a thick-walled reactor vessel a solution of **2** (0.480 g; 3.62 × 10^{-4} mol) in THF (10 mL) was subjected to several freeze–pump–thaw cycles. At room temperature, the reactor was charged with 4 atm CO gas and stirred for 1 h. The solution developed a red–amber colour during this time. The volatiles were removed *in vacuo* and the orange residue was recrystallized from Et_2O (2 mL) under CO and a few drops of toluene to give deep amber plates of **6**[BAr$_4$] (0.200 g; 33% yield). ^1H NMR ([$^2H_8$]THF, 500.13 MHz): δ 7.79 (br s, 8 H, *o*-H of Ar_4), 7.51 (br s, 4 H, *p*-H of Ar_4), 2.38–2.25 (m, 8 H, C*H*MeMe′), 1.97 (m, 8 H, PCH_2CH_2P), 1.49, 1.39, 1.25 and 1.19 (m, 48 H, CH*MeMe*′), 0.55 (m, 3 H, Pd–Me). ^{31}P-{^1H} NMR ([$^2H_8$]THF, 202.42 MHz): δ 58.6; at −70 °C, 68.5, 64.5, 59.0, 58.0 (Found: C, 48.05; H, 4.95. Calc. for $C_{69}H_{86}BF_{24}OP_4Pd_2$ *i.e.* {[Pd(dippe)CO][Pd(dippe)Me]}[BAr$_4$]·C_7H_8: C, 47.74; H, 5.05%).

Similarly was prepared **6**-$^{13}C_1$ with **2**-$^{13}C_1$ (0.050 g; 4.01 × 10^{-5} mol) in [$^2H_8$]THF (0.4 mL). The product was characterized in solution. ^{31}P-{^1H} NMR ([$^2H_8$]THF, 81.015 MHz): δ 58.6 (d, J_{PC} = 14.6 Hz). ^{13}C-{^1H} NMR ([$^2H_8$]THF, 50.32 MHz): δ 47.3 (qnt, Pd–Me, J_{CP} = 14.6 Hz); ^{13}C NMR (q of qnt, Pd–Me, J_{HC} = 127.6, J_{CP} = 14.6 Hz). Similarly was prepared **6a** with **2** (0.050 g; 4.01 × 10^{-5} mol) in [$^2H_8$]THF (0.4 mL). The product was characterized in solution under ^{13}CO. ^{31}P-{^1H} NMR ([$^2H_8$]THF, 202.42 MHz): δ 58.7 (dd, J_{PC} = 28.2, $J_{PC'}$ = 25.6 Hz). ^{13}C-{^1H} NMR ([$^2H_8$]THF, 50.32 MHz): δ 236.4 (qnt, CO, J_{CP} = 28.2), 228.1 (qnt, CO, $J_{C'P}$ = 25.6 Hz).

[Pd(dippe)(CO^{13}CH$_3$)CO][BAr$_4$] 7[BAr$_4$]. In a 5 mm NMR tube, **2**-$^{13}C_1$ (0.030 g; 2.27 × 10^{-5} mol) was dissolved in Et_2O (0.4 mL) and a few drops of C_6D_6 were added. The solution was freeze–pump–thawed, sealed under *ca.* 2 equivalents of carbon monoxide, and its ^{31}P-{^1H} and ^{13}C-{^1H} NMR spectra were recorded. ^{31}P-{^1H} NMR (C_6D_6–Et_2O, 81.015 MHz): δ 73.7 (dd, 1 P, $J_{PP'}$ = 40.6, J_{CP} = 38.7), 70.7 (dd, 1 P, $J_{PP'}$ = 40.6, J_{CP} = 17.3 Hz). ^{13}C-{^1H} NMR (C_6D_6–Et_2O, 50.32 MHz): δ 47.3 [dd, $CO^{13}CH_3$, J_{CP} (*trans*) = 38.7 Hz, $J_{CP'}$ (*cis*) = 17.3 Hz].

[Pd(dippe)(^{13}CH$_3$)CO][BAr$_4$] 8[BAr$_4$]. In a 5 mm NMR tube, **2** (0.030 g; 2.27 × 10^{-5} mol) was dissolved in $C_6D_4Cl_2$-*o* (0.35 mL). The solution was freeze–pump–thawed, sealed under *ca.* 2 equivalents of carbon monoxide, and its ^{31}P-{^1H} and ^{13}C-{^1H} NMR spectra were recorded. ^{31}P-{^1H} NMR ($C_6D_4Cl_2$-*o*, 81.015 MHz): δ 84.2 (dd, 1 P, $J_{PP'}$ = 21.2, J_{CP} = 105), 83.8 (dd, 1 P, $J_{PP'}$ = 21.2, J_{CP} = −8.5 Hz). ^{13}C-{^1H} NMR ($C_6D_4Cl_2$-*o*, 50.32 MHz): δ −4.9 [dd, Pd–CH_3, J_{CP} (*trans*) = 105, $J_{CP'}$ (*cis*) = −8.5 Hz].

[Pd(dippe)(CO)$_2$][BAr$_4$]$_2$ 9[BAr$_4$]$_2$, [Pd(dippe)(N≡CCH$_3$)$_2$][BAr$_4$]$_2$ 10a[BAr$_4$]$_2$ and [Pd(dippe)(THF)$_2$][BAr$_4$]$_2$ 10b[BAr$_4$]$_2$. To a solid mixture of HBAr$_4$ (0.416 g; 4.11 × 10^{-4} mol) and Pd(dippe)Me$_2$ (0.133 g; 2.06 × 10^{-4} mol) under vacuum at −196 °C, was added THF (2.0 mL) by trap to trap distillation. The reaction vessel was backfilled with CO (*ca.* 20 equivalents) and allowed to warm to −78 °C, at which temperature a clear yellow solution was observed. The solvent was removed *in vacuo* at −20 °C and [Pd(dippe)(CO)$_2$][BAr$_4$]$_2$ **9**[BAr$_4$]$_2$ was characterized in solution. ^{31}P-{^1H} NMR (CD_2Cl_2, 121.42 MHz): δ 83.8. The residue of the reaction mixture was recrystallized from methylene chloride (2 mL) and cooled to −40 °C. Yellow crystals of [Pd(dippe)(THF)$_2$][BAr$_4$]$_2$ **10b** appeared after 12 h (0.220 g; 25%). ^1H NMR (CD_2Cl_2, 500.13 MHz): δ 7.64 (br s, 16 H, *o*-H of Ar_4), 7.49 (br s, 8 H, *p*-H of Ar_4), 3.86 (m, 8 H, OCH_2CH_2), 2.32 (spt, 4 H, C*H*MeMe′, J_{HMe} = 7.3), 2.17 (m, 4 H, $PCH_2CH'_2P$), 1.97 (m, 8 H, OCH_2CH_2), 1.36 and 1.28 (dd, 24 H, CH*MeMe*′, J_{MeP} = 18.5, J_{MeH} = 7.3 Hz). ^{31}P-{^1H} NMR (CD_2Cl_2, 202.42 MHz): δ 118.9 {Found: C, 45.48; H, 2.97. Calc. for $C_{82}H_{64}B_2F_{48}OP_2Pd$ *i.e.* [Pd(dippe)(THF)][BAr$_4$]$_2$: C, 45.44; H, 2.98%}. [Pd(dippe)(N≡CCH$_3$)$_2$][BAr$_4$]$_2$ **10a**[BAr$_4$]$_2$ was prepared by adding CD_3CN (1 mL) to a mixture of HBAr$_4$ (0.102 g; 5.01 × 10^{-5} mol) and Pd(dippe)Me$_2$ (0.020 g; 2.50 × 10^{-5} mol), and characterized in solution. ^1H NMR (CD_3CN, 200.13 MHz): δ 7.71 (br s, 16 H, *o*-H of Ar_4), 7.66 (br s, 8 H, *p*-H of Ar_4), 2.57 (spt, 4 H, C*H*MeMe′, J_{HMe} = 7.3), 2.31 (m, 4 H, $PCH_2CH'_2P$), 1.38 and 1.30 (dd, 24 H, CH*MeMe*′, J_{MeP} = 15.0, J_{MeH} = 7.3 Hz). ^{31}P-{^1H} NMR (CD_3CN, 81.015): δ 118.9.

[Pd(dippp)(μ-CO)Pd(dippe)Me][BAr$_4$] 11[BAr$_4$]. To a solution of Pd(dippp)CO {prepared from [Pd(dippp)]$_2$ (0.015 g; 2.00 × 10^{-5} mol) under CO in 5 mL Et_2O} was added **2** (0.050 g; 4.01 × 10^{-5} mol). The product was characterized in solution. ^{31}P-{^1H} NMR (C_6D_6, 81.015 MHz): δ 53.8 (t, 1 P, $J_{PP'}$ = 28.5), 23.8 (t, 1 P, $J_{P'P}$ = 28.5 Hz).

X-Ray crystallographic analysis of [(dippe)Pd(μ-CO)Pd(dippe)Me]{B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$}·0.5C$_7$H$_8$ 6

Crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with 2θ = 20.0–22.9°. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, decayed linearly by 22.5%. The data were processed[52] and corrected for Lorentz and polarization effects, decay and absorption (empirical, based on azimuthal scans).

The structure was solved by direct methods. The structure analysis was initiated in the centrosymmetric space group $P\bar{1}$, this choice being confirmed by subsequent calculations. The C(53) trifluoromethyl group was modelled as 1 : 1 disordered. Several more CF_3 groups and the Pd(2) chelate ring show signs of minor disordering, but the quality of the data set was not sufficient to permit full modelling of this disorder. The toluene solvent is disordered in a complex fashion about a centre of symmetry; no models having reasonable geometry could be refined successfully. The seven largest peaks in the toluene region were refined as carbon atoms with occupancy factors constrained to total 3.5 and thermal parameters constrained to be approximately equal. All non-hydrogen atoms except C(63) and C(69) (which had non-positive definite thermal parameters when refined anisotropically) were refined with anisotropic thermal parameters. The hydrogen atoms associated with the cation and the anion were fixed in calculated positions with C–H = 0.98 Å and $B_H = 1.2\ B_{\text{bonded atom}}$ while those associated with the toluene molecule were not included in the model. No secondary extinction correction was necessary. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref. 53.

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References

1 P. M. Maitlis, *The Organic Chemistry of Palladium*, Academic Press, New York, London, 1971.
2 G. W. Parshall and S. D. Ittel, *Homogeneous Catalysis*, John Wiley and Sons, New York, 1992.
3 A. Sen and T. W. Lai, *J. Am. Chem. Soc.*, 1982, **104**, 3520.
4 A. Sen, *Acc. Chem. Res.*, 1993, **26**, 303.
5 E. Drent, J. A. M. v. Broekhoven and M. J. Doyle, *J. Organomet. Chem.*, 1991, **417**, 235.
6 E. Drent, *Pure Appl. Chem.*, 1990, **62**, 661.
7 M. Brookhart, M. Grant and A. F. Volpe, jun., *Organometallics*, 1992, **11**, 3920.
8 M. Brookhart, F. C. Rix, J. M. DeSimone and J. C. Barborak, *J. Am. Chem. Soc.*, 1992, **114**, 5894.
9 M. Brookhart, M. I. Wagner, G. G. Balavoine and H. A. Haddou, *J. Am. Chem. Soc.*, 1994, **114**, 3641.
10 F. C. Rix and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 1137.
11 F. C. Rix, M. Brookhart and P. S. White, *J. Am. Chem. Soc.*, 1996, **118**, 4746.
12 L. K. Johnson, S. Mecking and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 267.
13 L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414.
14 Z. Jiang and A. Sen, *J. Am. Chem. Soc.*, 1995, **117**, 4455.
15 C. Pisano, G. Consiglio, A. Sironi and M. Moret, *J. Chem. Soc., Chem. Commun.*, 1991, 421.
16 A. Batistini and G. Consiglio, *Organometallics*, 1992, **11**, 1766.
17 C. Pisano, S. C. A. Nefkens and G. Consiglio, *Organometallics*, 1992, **11**, 1975.
18 M. Barsacchi, G. Consiglio, L. Medici, G. Petrucci and U. W. Suter, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 989.
19 A. Batistini, G. Consiglio and U. W. Suter, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 303.
20 S. Bronco, G. Consiglio, S. D. Benedetto, M. Fehr, F. Spindler and A. Togni, *Helv. Chim. Acta*, 1995, **78**, 883.
21 For specific accounts of carbonylation reactions of metal alkyls, see: F. Calderazzo, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 299; E. J. Kuhlmann and J. J. Alexander, *Coord. Chem. Rev.*, 1980, **33**, 195; G. K. Anderson and R. J. Cross, *Acc. Chem. Res.*, 1984, **17**, 67.
22 M. D. Fryzuk, B. R. Lloyd, G. K. B. Clentsmith and S. R. Rettig, *J. Am. Chem. Soc.*, 1994, **116**, 3804.
23 M. D. Fryzuk, G. K. B. Clentsmith, G. Hägele and S. J. Rettig, *Organometallics*, 1996, **15**, 2083.
24 M. D. Fryzuk, D. H. McConville and S. J. Rettig, *J. Organomet. Chem.*, 1993, **445**, 245.
25 F. A. Cotton and T. J. Marks, *J. Am. Chem. Soc.*, 1969, **91**, 1339.
26 X. Yang, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10 015.
27 P. W. Jolly, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 283.
28 F. Ozawa, T. Hayashi, H. Koide and A. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1991, 1469.
29 G. P. C. M. Dekker, C. J. Elsevier, K. Vrieze and P. W. N. M. van Leeuwen, *Organometallics*, 1992, **11**, 1598.
30 G. P. C. M. Dekker, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen and C. F. Roobeek, *J. Organomet. Chem.*, 1992, **430**, 357.
31 I. Tóth and C. J. Elsevier, *J. Chem. Soc., Chem. Commun.*, 1993, 529.
32 P. W. N. M. van Leeuwen, C. F. Roobeck and H. v. d. Heijden, *J. Am. Chem. Soc.*, 1994, **116**, 12 117.
33 For reviews on CO/alkene polymerization, see: A. Sen, *Adv. Polym. Sci.*, 1986, **73/74**, 125; E. Drent, *Chem. Rev.*, 1996, **96**, 663.
34 A. L. Seligson and W. C. Trogler, *J. Am. Chem. Soc.*, 1991, **113**, 2520.
35 H. B. Davis, F. W. B. Einstein, P. G. Glavina, T. Jones, R. K. Pomeroy and P. Rushman, *Organometallics*, 1989, **8**, 1030.
36 F. A. Cotton, *Prog. Inorg. Chem.*, 1976, **21**, 1.
37 An alternative formulation of **6a**, as [Pd(dippe)(μ-^{13}CO)Pd(dippe)(^{13}COMe)]$^+$, *i.e.* a dinuclear system bridged by CO, and having an acetyl group, is untenable due to the observed ^{13}C-{^{1}H} NMR spectrum of **2**-$^{13}C_1$ under ^{13}CO: $J_{CC'}$ values of 4–10 Hz are measured; therefore the scalar coupling is not of the $^1J_{CC'}$ type [*cf.* $^1J_{CC} = 40.6$ Hz for the AX_2 pattern of $^{13}CH_3(^{13}CO)CH_3$, which is observed in the same spectrum] and a formulation of [Pd(dippe)(μ-^{13}CO)$_2$Pd(dippe)Me]$^+$ is justified.
38 M. Portnoy and D. Milstein, *Organometallics*, 1993, **12**, 1655.
39 M. Portnoy, F. Frolow and D. Milstein, *Organometallics*, 1991, **10**, 3960.
40 M. Portnoy and D. Milstein, *Organometallics*, 1994, **13**, 600.
41 I. Tóth and C. J. Elsevier, *J. Am. Chem. Soc.*, 1993, **115**, 10 388.
42 T. Yamamoto, T. Kohara and A. Yamamoto, *Chem. Lett.*, 1976, 1217.
43 B. A. Markies, P. Wijkens, A. Dedieu, J. Boersma, A. L. Spek and G. van Koten, *Organometallics*, 1995, **14**, 5628.
44 A. Sen, *CHEMTECH*, 1986, 48.
45 J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987.
46 M. E. Thompson, S. M. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. P. Schaefer and J. E. Bercaw, *J. Am. Chem. Soc.*, 1987, **109**, 203.
47 P. Burger and R. G. Bergman, *J. Am. Chem. Soc.*, 1993, **115**, 10 462.
48 B. A. Arndtsen and R. G. Bergman, *Science*, 1995, **270**, 1970.
49 A. G. Massey and A. Park, *J. Organomet. Chem.*, 1966, **5**, 218.
50 N. H. Dryden, P. Legzdins, J. Trotter and V. C. Yee, *Organometallics*, 1991, **10**, 2857.
51 R. E. Rülke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. W. N. M. van Leeuwen and K. Vrieze, *Inorg. Chem.*, 1993, **32**, 5769.
52 TEXSAN, Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1995.
53 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99–102 (present distributor Kluwer Academic Publishers, Boston, MA); *International Tables for Crystallography*, Kluwer Academic Publishers, Boston, MA, 1992, vol. C, pp. 200–206.

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