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Stepwise substitution of terminal and bridging phosphines in $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)(PBu^t_2H)_2]BF_4$ and the reactivity of $[Pd_2(\mu\text{-}PBu^t_2)(PPh_3)_3]BF_4$

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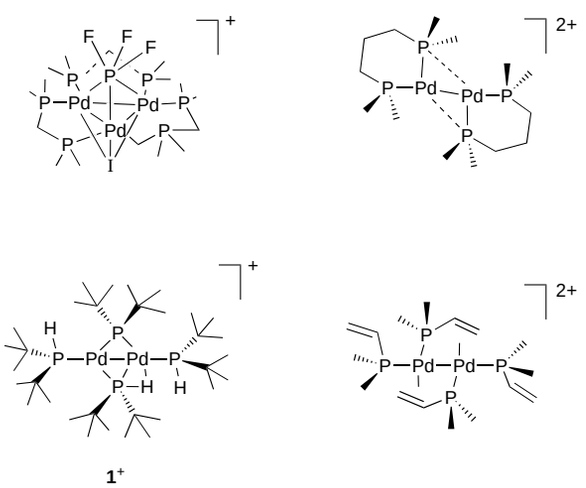
The dipalladium(I) cationic complex $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)(PBu^t_2H)_2]BF_4$ **1**, with a central $[Pd_2(\mu\text{-}PBu^t_2)]^+$ core binding two different types of PBu^t_2H molecules, was treated with tertiary phosphines (PR_3, R = Me, Et, Ph or C_6H_4OMe-2). The terminally bonded PBu^t_2H molecules were substituted under mild conditions yielding the new derivatives $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)(PR_3)_2]BF_4$, which still bear a bridging secondary phosphine. The latter can be substituted under more forcing conditions which allow the isolation of the persubstituted $[Pd_2(\mu\text{-}PBu^t_2)(PR_3)_n]BF_4$. The reactions of one of these derivatives, $[Pd_2(\mu\text{-}PBu^t_2)(PPh_3)_3]BF_4$, with CO, MeCN or isoprene giving, respectively, $[Pd_2(\mu\text{-}PBu^t_2)(PPh_3)_3L]BF_4$ (L = CO or MeCN) or $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}CH_2{=}CHCMe{=}CH_2)(PPh_3)_2]BF_4$ are also described.

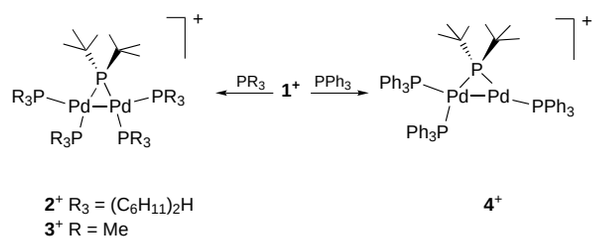
Mono- and poly-dentate phosphines are ligands of widespread use in organometallic chemistry.[1] Since the origin of this science, and up to a few years ago, a common viewpoint was that monodentate phosphines act exclusively as two-electron terminally bonded donors. Polyphosphines were known to chelate a single metal center or also to bridge two or more metals, but always in what could be defined the 'classical way', *i.e.* with each phosphorus interacting with only one metal. A few, but persuasive, recent reports suggest that exceptions can be found to this general rule; curiously enough all examples involve palladium, but this is probably only by chance.

A first contribution came from Balch *et al.*[2a] who prepared in 1990 the cluster $[Pd_3(\mu\text{-dppm})_3(\mu_3\text{-I})(\mu_3\text{-}PF_3)]PF_6$ [dppm = bis(diphenylphosphino)methane] (Chart 1), crystallographically



1$^+$

shown to contain a PF_3 molecule triply bridging a central triangular Pd_3 core. However, exceptions are not limited to PF_3, an atypical phosphine often considered closer to carbon monoxide. Subsequently the structure of $[Pd_2(dppp)_2][CF_3SO_3]_2$ [dppp = 1,3-bis(diphenylphosphino)propane] was reported[3] which contains a dinuclear palladium(I) cation, surviving thanks to a metal–metal bonding interaction, *and* two bridging phosphines. The cation can in fact be viewed as the dimer of the bent $(dppp)Pd^+$ moiety; within each dppp molecule one phosphorus binds terminally one of the metals and the remaining one bridges the Pd–Pd bond. *Ab initio* calculations on the model $[\{Pd(PH_3)_2\}_2]^{2+}$ cation show[3] that the phosphorus bridges are not assisted by interactions of the metal centers with the phosphine's phenyl substituents.



2$^+$ $R_3 = (C_6H_{11})_2H$
3$^+$ R = Me
4$^+$

Scheme 1

Further conceptually related examples are $[Rh_2Cl_2(\mu\text{-}CR_2)_2(\mu\text{-}SbR'_3)_2]$ containing a triply bridging stibine,[4] and other derivatives[5] containing a $\mu_3\text{-}PR_2$ ligand. Our group provided a further contribution to this field by preparing the secondary phosphine-bridged $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)(PBu^t_2H)_2]BF_4$ **1**.[6] With respect to most of the bridges described above, which involve orbitals centered on single phosphorus atoms, the bridging secondary phosphine in $\mathbf{1}^+$ differs substantially because of the active role played by the P–H σ bond. This furnishes two extra electrons, involved in an unprecedented Pd–H–P agostic interaction, to the dimetallic system. The PBu^t_2H molecule can therefore be formally considered as a $4e^-$ donor, or, in other words, a bidentate ligand, as for example the bridging diphenylvinylphosphine in the cation $[\{Pd[\mu\text{-}PPh_2(CH{=}CH_2)][PPh_2(CH{=}CH_2)]\}_2]^{2+}$.[7] Owing to the weak contribution given by the Pd–H–P interaction, the bridging PBu^t_2H molecule is not as tightly bonded as other bridging bidentate ligands, as for example the widely employed dppm[8] molecule. This can easily be confirmed by comparing the reactivities of **1** and of its derivative $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-dppm})(PBu^t_2H)_2]BF_4$[9] with monodentate phosphines. The latter was found to react with tertiary phosphines yielding new $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-dppm})(PR_3)_2]BF_4$ derivatives,[9] with an unchanged Pd_2P_3 internal core. Conversely the reactions of **1** with $P(C_6H_{11})_2H$, PMe_3[10] or PPh_3[11] gave high yields of the derivatives $[Pd_2(\mu\text{-}PBu^t_2)(PR_3)_n]BF_4$ [Scheme 1; $n = 4$, $R_3 = (C_6H_{11})_2H$, **2**; R = Me **3**; $n = 3$, R = Ph **4**]. These were all obtained by operating under a large excess of the

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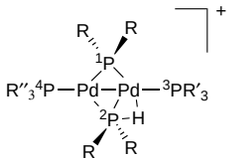
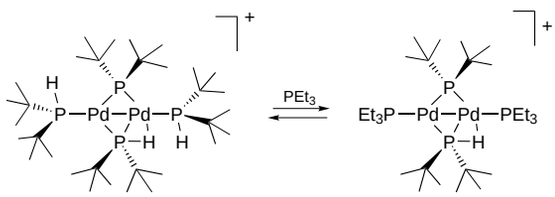
Table 1 Proton and ^{31}P-{^{1}H} NMR parameters (δ, *J*/Hz) of $[Pd_2(\mu\text{-}PR_2)(\mu\text{-}PR_2H)(PR'_3)(PR''_3)]BF_4$



	$\mathbf{1}^{+}$ [a]	$\mathbf{5}^{+}$ [b]	$\mathbf{6}^{+}$ [c]	$\mathbf{8}^{+}$ [d]	$\mathbf{9}^{+}$ [e]	$\mathbf{10}^{+}$ [f]
δ_{P1}	455.3	445.1	392.3	440.7	440.7	431.0
δ_{P2}	217.2	220.2	179.6	189.3	187.6	186.5
δ_{P3}	47.7	9.05	35.1	15.5	44.8	8.9
δ_{P4}	52.0	14.2	47.0	23.1	19.8	17.5
$^{2}J_{P1P2}$	190	184	185	190	196	199
$^{2}J_{P1P3}$	21	29	29	33	22	32
$^{2}J_{P1P4}$	49	54	55	56	57	54
$^{2}J_{P2P3}$	96	99	110	87	92	91
$^{2}J_{P2P4}$	15	26	29	19	20	18
$^{3}J_{P3P4}$	65	73	66	79	65	83
δ_{H}	−0.16	−0.44	−0.35	−0.49	*g*	0.15
$^{1}J_{P2H}$	151	146	136	159	*g*	161
$^{2}J_{P2H}$	35	39	40	33	*g*	34

[a] R = Bu^t, R′$_3$ = R″$_3$ = Bu^t_2H. [b] R = Bu^t, R′ = R″ = Et. [c] R = C_6H_{11}, R′$_3$ = R″$_3$ = $(C_6H_{11})_2Et$. [d] R = Bu^t, R′ = R″ = Ph. [e] R = Bu^t, R′$_3$ = Bu^tH, R″$_3$ = $Ph(C_6H_4OMe\text{-}2)_2$. [f] R = Bu^t, R′$_3$ = R″$_3$ = $Ph(C_6H_4OMe\text{-}2)_2$. [g] Not measured.



Scheme 2

entering phosphine, which allowed the substitution of *all* the PBu^t_2H molecules contained in cation $\mathbf{1}^{+}$. As will be described in this paper, the intermediate complexes $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)(PR_3)_2]BF_4$ arising from the selective substitution of the terminally bonded secondary phosphines of **1** can be isolated in good yields and purity. This suggests that the strength of the overall $Pd_2(\mu\text{-}PBu^t_2H)$ interaction is greater than that of a terminal Pd–PBu^t_2H bond, and opens a way to the achievement of numerous new phosphine-bridged derivatives. Some aspects of the reactivity of one of the previously reported per-substituted derivatives, $[Pd_2(\mu\text{-}PBu^t_2)(PPh_3)_3]BF_4$, will also be described.

Results and Discussion

Reactions of complex 1 with PEt_3

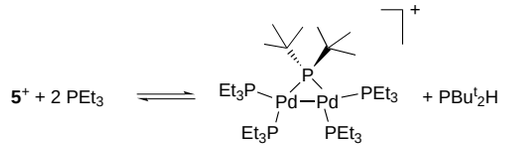
As pointed out in the introduction, we knew that **1** reacts with an excess of PR_3 [$R_3 = (C_6H_{11})_2H$, R = Me or Ph][10,11] yielding the corresponding products of complete substitution of the PBu^t_2H molecules. In an attempt to prepare the corresponding persubstituted derivative, we treated **1** with a six-fold excess of PEt_3. The deep violet CH_2Cl_2 solution of **1** turned to purple-red after 30 min from the addition of the tertiary phosphine. A sample of the solution was analysed by ^{31}P-{^{1}H} NMR spectroscopy which clearly showed the presence of a single product arising from substitution of only the terminally bonded secondary phosphines. The shape of the spectrum allowed us safely to assign the composition $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)(PEt_3)_2]BF_4$, **5**, to the new complex (Scheme 2). The spectrum is in fact very similar to the corresponding, highly diagnostic, spectrum of the starting material.[6] Four groups of resonances were in fact observed at δ 445.1, 220.2, 14.2 and 9.05, together with a strong singlet at δ −17.2 for the free excess of PEt_3. The four resonances assigned to **5** all appear as doublets of doublets of doublets (see Table 1 for the numbering scheme and the complete list of coupling constants). Both chemical shifts and coupling constants of the two low-field resonances compare well to the corresponding signals given by **1**[6] and by the related $[Pd_2\{\mu\text{-}P(C_6H_{11})_2\}\{\mu\text{-}P(C_6H_{11})_2H\}\{P(C_6H_{11})_2Et\}_2]BF_4$ **6**,[10] which were assigned, respectively, to the bridging phosphide and to the bridging phosphine.

The proton-coupled ^{31}P NMR spectrum showed a relatively small broadening of all the signals but that at δ 220.2, which split into a broad doublet by virtue of the large value of $^{1}J_{PH} = 146$ Hz. As observed before, the latter value is sensibly reduced with respect to the 'normal' values of $^{1}J_{PH}$ (*ca.* 300–360 Hz) of terminally bonded secondary phosphines.[6,10] The new complex was isolated in 92% yield as a purple-red microcrystalline solid, which analysed nicely for the structure **5** and gave a ^{1}H NMR spectrum with a doublet of doublets centred at δ −0.44 ($^{1}J_{PH} = 146$, $^{2}J_{PH} = 39$ Hz). This, being intermediate between the δ_{PH} values of terminally bonded secondary phosphines and of metal hydrides arising from complete oxidative addition of the P–H bond, is diagnostic for the presence of a Pd–H–P three-centre two-electron interaction. For comparison, the analogous values for **1** and **6** were δ_{PH} −0.16 and −0.35, $^{1}J_{PH} = 151$ and 136 Hz and $^{2}J_{PH} = 35$ and 40 Hz.[6,10] Similar results and yields were obtained when the reaction was performed with a two-fold excess of PEt_3.

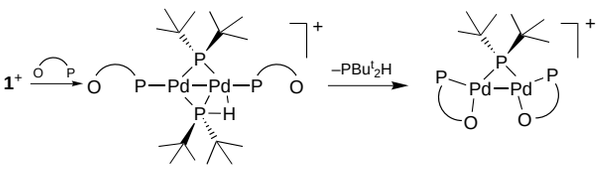
When complex **5** was dissolved in CH_2Cl_2 in the presence of a 10-fold excess of triethylphosphine the ^{31}P-{^{1}H} NMR spectrum of the solution exhibited, besides the resonances discussed above, two broad, featureless signals centred around δ 318 and 0. At low temperature (188 K) the same sample displayed, sufficiently resolved, the resonances of the new complex, and two singlets at δ 19 and −17, assignable, respectively, to free PBu^t_2H and PEt_3, while the resonances attributed to **5** had completely disappeared. The new signals, very similar to those previously observed for $[Pd_2(\mu\text{-}PBu^t_2)(PMe_3)_4]BF_4$, **3**,[10] were a complex triple multiplet at δ 333 ($^{2}J_{PP}$ *ca.* 185 and 40 Hz),‡ and two broad doublets at δ −1.6 ($^{2}J_{PP}$ *ca.* 185) and −3.0 ($^{2}J_{PP}$ *ca.* 40 Hz); these were assigned, respectively, to the bridging phosphide (C), to two PEt_3 molecules lying pseudo-*trans* (AA′) and to two lying pseudo-*cis* (BB′) to μ-P in $[Pd_2(\mu\text{-}PBu^t_2)(PEt_3)_4]BF_4$ **7** (spin system: AA′BB′C) and were only slightly broadened in the corresponding proton-coupled spectrum, none of them showing the typical splitting due to $^{1}J_{PH}$ for secondary phosphines.

These data are satisfactorily explained by the equilibrium in Scheme 3, which is shifted far towards the reagents. Complex **7** is in fact observed only in the presence of a large excess of PEt_3 and preferably at low temperatures which further shift the equilibrium to the right, reasonably due to an unfavorable entropic contribution. Moreover, the previous observation that the reactions of **1** with a small excess of PMe_3 or $P(C_6H_{11})_2H$ are completely shifted toward the corresponding $[Pd_2(\mu\text{-}PBu^t_2)(PR_3)_4]BF_4$ derivatives suggests a great dependence of Pd–PR_3 bond energies on the steric bulkiness of the phosphine, which

‡ The complexity of the low-field signal (at least 12 lines) arising from the fact that, as shown before for the PMe_3 derivative,[10] this absorption is best considered as the C part of an AA′BB′C spin system, despite the large difference between the two regions of the spectrum. This can be clearly seen by computer simulations of the spectrum which reproduce the gross features, however the simulation has not been optimized since none of the nine variables (which grow to 15 by taking into account the signs of the coupling constants) can be directly obtained from the spectra. The coupling constants and chemical shifts given must therefore be considered approximate.



Scheme 3



Scheme 4

sounds very reasonable for these highly hindered systems. Other facts among the previously reported body of data show that the co-ordination ability of the central triangular $[Pd_2(\mu\text{-}PBu^t_2)]^+$ core is greatly influenced by the shape of the ligands.[6,10–12]

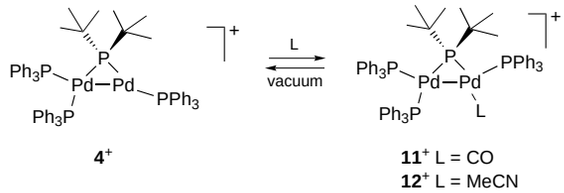
Another important suggestion arising from the above results is that the reactions of complex **1** with other phosphines proceed, under appropriate conditions, through *isolable* intermediates which still bear a *bridging* PBu^t_2H molecule. The following results confirm this hypothesis.

Reactions of complex 1 with PPh_3

A 10-fold excess of PPh_3 was added to a CH_2Cl_2 solution of complex **1**. A sample of the solution was analysed by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy which revealed only the resonances of a new derivative; chemical shift and coupling constants values, given in Table 1 and fully comparable to the corresponding values found for **1**, **5** and **6**, clearly correspond to the formula $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)(PPh_3)_2]BF_4$, **8**. The latter was isolated (85% yield) as a purple microcrystalline solid, similar yields being obtained starting from a two-fold excess of PPh_3. All other analyses (see Experimental section) confirmed the formulation. At room temperature complex **8** is stable also in the presence of a larger excess of PPh_3, but warming for 12 h at 70 °C in the presence of a 10-fold excess of PPh_3 gave (90%) the known[11] persubstituted derivative $[Pd_2(\mu\text{-}PBu^t_2)(PPh_3)_3]BF_4$ **4**. As reported previously[11] it proved impossible to add a fourth molecule of triphenylphosphine to the formally unsaturated **4**.

Reactions of complex 1 with $PPh(C_6H_4OMe\text{-}2)_2$

The potentially bidentate phosphine $PPh(C_6H_4OMe\text{-}2)_2$ can function as an hemilabile ligand which can temporarily stabilize a reactive unsaturated center through the co-ordination of the methoxy group.[13] It was therefore treated with complex **1** with the intent to construct new systems with the reactive $[Pd_2(\mu\text{-}PBu^t_2)(PR_3)_2]^+$ fragment less firmly protected than in the starting material (Scheme 4). A 10-fold excess of $PPh(C_6H_4OMe\text{-}2)_2$ was added in a NMR tube to a 1,2-dimethoxyethane solution of **1**, and the progress of the reaction was monitored by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. The reaction was very slow, and, after 12 h at 75 °C, the starting material was converted into a mixture of $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)(PBu^t_2H)\{PPh(C_6H_4OMe\text{-}2)_2\}]BF_4$ **9**, and $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)\{PPh(C_6H_4OMe\text{-}2)_2\}_2]BF_4$ **10**. The solution was left for 7 d at 75 °C, when only a small amount of **9** was still present. The structures of the cations $\mathbf{9}^+$ and $\mathbf{10}^+$ can now be straightforwardly assigned by comparison of the spectra with those of the analogous complexes described previously (Table 1). The reaction was repeated at higher temperatures in a flask. A six-fold excess of $PPh(C_6H_4OMe\text{-}2)_2$ was added to a solution of complex **1** in Bu^n_2O; after 24 h at 110 °C complex **10** was isolated in 70% yield. Subsequent attempts to remove the bridging phosphine and isolate PO chelate complexes as shown in Scheme 4 were unsuccessful, always giving complex mixtures.



Scheme 5

Reactivity of complex 4

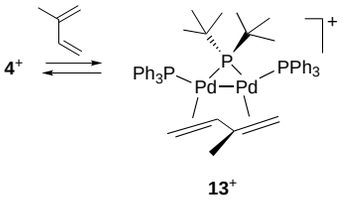
The synthesis of complex **4** had been briefly communicated, together with its employment in the preparation of an interesting complex exhibiting an unprecedented mode of co-ordination of the CS_2 molecule.[11] The reactions of **4** with monodentate ligands, and with isoprene will now be described.

With CO and MeCN. When carbon monoxide was bubbled through a NMR tube containing a red solution of complex **4** in $(CD_3)_2CO$, the solution turned to yellow in a few minutes. The resonances of the starting material disappeared completely from the $^{31}P\text{-}\{^1H\}$ NMR spectrum, which exhibited four new doublets of doublets of doublets at δ 335.1 (J_{PP} = 193, 36, 19), 22.1 (J_{PP} = 193, 42, 14), 14.2 (J_{PP} = 36, 42, 177) and 5.62 (J_{PP} = 19, 14, 177 Hz). The spectrum is consistent with the presence of a central metal–metal bonded $Pd_2(\mu\text{-}PBu^t_2)$ core substituted with two PPh_3 molecules in pseudo-*cis* and one in pseudo-*trans* position with respect to the bridging phosphorus. The large value of $^2J_{PP}$ = 193 Hz is in fact typical of *trans*-PP coupling constants, and values as large as that of $^3J_{PP}$ = 177 Hz have frequently been observed in these types of structures. The IR spectrum of the solution showed a strong absorption at 2071 cm^{-1}, consistent with the presence of a terminally bonded carbonyl ligand. Both $^{31}P\text{-}\{^1H\}$ NMR coupling patterns and IR data compare well with those given by the monocarbonyls $[Pd_2(\mu\text{-}PBu^t_2)(PR_3)_3(CO)]BF_4$ [$R_3 = (C_6H_{11})_2H$, R = Me].[12b]

These data can be safely explained by the structure $[Pd_2(\mu\text{-}PBu^t_2)(PPh_3)_3(CO)]BF_4$, **11**, shown in Scheme 5 and arising from the co-ordination of a CO molecule to the unsaturated center of the reactant. This reaction is fully reversible by simply bubbling N_2 through the NMR tube. It was repeated in a flask and showed analogous behaviour; the complex can be isolated as a yellow-orange solid, but is converted quantitatively to **4** if vacuum drying is attempted.

The same type of reaction was observed with MeCN which gives a new product, with resonances at δ 324 (J_{PP} = 179, 37, 44), 25.3 (J_{PP} = 179, 22, 19), 11.7 (J_{PP} = 19, 44, 198) and 8.02 (J_{PP} = 37, 22, 198 Hz) in the $^{31}P\text{-}\{^1H\}$ NMR spectrum, and identified as $[Pd_2(\mu\text{-}PBu^t_2)(PPh_3)_3(NCMe)]BF_4$ **12**. Also in this case a lemon-yellow solid was isolated at the end of the reaction but was slowly converted back into **4** during the drying process *in vacuo*.

With isoprene. We had previously shown that either complex **1**[12a] or its derivatives[12b] **2** and **3** react reversibly with isoprene yielding the corresponding derivatives with the $[Pd(\mu\text{-}PBu^t_2)]^+$ core which co-ordinates two phosphine ligands and the diene molecule, the latter opposing the phosphido bridge. A similar reaction has been observed with **4**. By addition of a seven-fold excess of isoprene, a red acetone solution of **4** turned immediately yellow. After work-up we isolated in 91% yield the diene complex $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}CH_2{=}CHCMe{=}CH_2)(PPh_3)_2]BF_4$ **13** (Scheme 6), as a yellow solid. In strict analogy to the spectra of the corresponding $P(C_6H_{11})_2H$ and PMe_3 derivatives,[12] three groups of resonances were observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **13** at δ 352, 16.8 and 15.8. The first (triplet, $^2J_{PP}$ = 34 Hz) was assigned to the bridging phosphide



13^+

Scheme 6

coupled to the two *cis* phosphine molecules. These are slightly different, due to the asymmetry of the diene ligand, and give the two high-field signals as an AB spin subsystem (two distorted overlapping doublets of doublets, which furnish the values of $^2J_{PP} = 34$ and $^3J_{PP} = 68$ Hz). The presence of a co-ordinated isoprene molecule is confirmed by the ^{1}H NMR spectrum (see Experimental section) which also confirms the expected non-equivalence of the *tert*-butyl substituents on the bridging phosphide (two separate signals at δ 0.71 and 0.82).

Experimental

General

All reactions were performed under an atmosphere of purified nitrogen or carbon monoxide by using standard Schlenk techniques. Solvents were dried by standard procedures and distilled under nitrogen prior to use. Deuteriated solvents were used as received and stored over molecular sieves under an inert atmosphere. The compound $PPh(C_6H_4OMe\text{-}2)_2$,[14] **1**[6] and **4**[11] were prepared as previously described. Infrared spectra were registered with a Perkin-Elmer FT-IR 1725X spectrophotometer and NMR spectra with a Varian Gemini 200BB spectrometer, frequencies being referenced to the residual signal of the deuteriated solvent (^{1}H, ^{13}C) or to external 85% H_3PO_4 (^{31}P). The progress of the reactions was monitored by means of ^{31}P-{^{1}H} NMR spectroscopy of small samples of the mixture, after adding a few drops of C_6D_6 for the lock signal and field homogeneity optimisation.

Preparations

$[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)(PEt_3)_2]BF_4$ 5. Triethylphosphine (0.22 cm^3, 1.49 mmol) was added to a violet solution of complex **1** (602 mg, 0.681 mmol) in CH_2Cl_2 (20 cm^3). After 30 min at room temperature the purple-red solution was concentrated to *ca*. 5 cm^3. Diethyl ether (15 cm^3) was slowly added dropwise and the purple microcrystalline **5** was filtered off and vacuum dried (520 mg, 0.629 mmol, 92.4% yield) (Found: C, 40.3; H, 8.35. Calc. for $C_{28}H_{67}BF_4P_4Pd_2$; C, 40.6; H, 8.16%). IR (Nujol KBr); 2341w [ν(P–H)] and 1057vs cm^{-1} [ν(B–F), unco-ordinated BF_4^-]. ^{1}H NMR (CD_2Cl_2, 298 K); δ 2.00 (m, 12 H, PCH_2CH_3), 1.34 (d, $^3J_{PH} = 7$, 18 H, C_4H_9), 1.28 (d, $^3J_{PH} = 9$, 18 H, C_4H_9), 1.15 (m, 18 H, PCH_2CH_3) and −0.44 (dd, $^1J_{PH} = 146$, $^2J_{PH} = 39$ Hz, 1 H, PH).

$[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)(PPh_3)_2]BF_4$ 8. Triphenylphosphine (150 mg, 0.572 mmol) was added to a violet suspension of complex **1** (230 mg, 0.26 mmol) in 1,2-dimethoxyethane (20 cm^3). The mixture was stirred for 2 h at room temperature. The resulting purple suspension was concentrated to *ca* 10 cm^3, Et_2O (15 cm^3) was added and the purple-red **8** was filtered off and vacuum dried (245 mg, 0.22 mmol, 85% yield (Found: C, 55.5; H, 6.01. Calc. for $C_{52}H_{67}BF_4P_4Pd_2$: C, 56.0; H, 6.05%). IR (Nujol, KBr): 3040w [ν(=C–H)], 2330w [ν(P–H)], 1490, 1460m [ν(C=C)] and 1059vs cm^{-1} [ν(B–F)]. ^{1}H NMR (CD_2Cl_2 298 K): δ −0.49 (dd, $^1J_{PH} = 159$, $^2J_{PH} = 33$, 1 H, PH), 1.00 (d, $^3J_{PH} = 12$, 18 H, C_4H_9), 1.10 (d, $^3J_{PH} = 15$ Hz, 18 H, C_4H_9) and 7.5 (m, 30 H, C_6H_5).

$[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)\{PPh(C_6H_4OMe\text{-}2)_2\}_2]BF_4$ 10. Complex **1** (177 mg, 0.2 mmol) was suspended in Bu^n_2O (20 cm^3) and $PPh(C_6H_4OMe\text{-}2)_2$ (387 mg, 1.2 mmol) added. The suspension was stirred for 24 h at 110 °C and cooled to room temperature leaving a red-brown suspension. After the addition of *n*-hexane (30 cm^3) the solid **10** was filtered off, vacuum dried and recrystallized from CH_2Cl_2–Et_2O. Yield 174 mg (70%) (Found: C, 54.1; H, 6.18. Calc. for $C_{56}H_{75}BF_4O_4P_4Pd_2$: C, 54.4; H, 6.12%). ^{1}H NMR (CD_2Cl_2, 298 K): δ 0.15 (dd, $^1J_{PH} = 161$, $^2J_{PH} = 34$, 1 H, PH), 1.01 (d, $^3J_{PH} = 14$, 18 H, C_4H_9), 1.05 (d, $^3J_{PH} = 18$, 18 H, C_4H_9), 3.4 (d, $^2J_{PH} = 6$ Hz, 12 H, OCH_3), 6.4 (m, 10 H, C_6H_4OMe) and 7.4 (m, 10 H, C_6H_5).

Reaction of complex 4

With CO. Complex **4** (188 mg, 0.154 mmol) was suspended in 1,2-dimethoxyethane (5 cm^3) under nitrogen. The flask was then evacuated and filled with 1 atm (*ca*. 10^5 Pa) of carbon monoxide. The solid was readily dissolved leaving in a few minutes an orange-yellow solution; this was monitored by IR and NMR spectroscopy which exhibited only the signals attributed to $[Pd_2(\mu\text{-}PBu^t_2)(PPh_3)_3(CO)]BF_4$ **11** (see Results and Discussion). By adding Et_2O (15 cm^3) an orange solid precipitated and was filtered off. It turned back to red under vacuum, and IR and NMR spectra indicated that **4** was quantitatively reformed

With MeCN. Complex **4** (195 mg, 0.16 mmol) was dissolved in MeCN (5 cm^3) giving a lemon-yellow solution. As reported in the Results and Discussion, ^{31}P-{^{1}H} NMR spectra exhibited only new resonances which were assigned to $[Pd_2(\mu\text{-}PBu^t_2)(PPh_3)_3(NCMe)]BF_4$ **12**. Most of the solvent was evaporated and Et_2O (40 cm^3) was added, causing the precipitation of a yellow solid which turned back to red under vacuum; IR and NMR spectra indicated that **4** was quantitatively reformed.

With isoprene. Complex **4** (344 mg, 0.282 mmol) was dissolved in acetone (20 cm^3) and isoprene (2 cm^3, 20 mmol) added. The solution quickly turned yellow. After 30 min it was concentrated to *ca*. half volume, Et_2O (40 cm^3) added and cooled to −20 °C with stirring. The complex $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}CH_2{=}CHCMe{=}CH_2)(PPh_3)_2]BF_4$ precipitated as a yellow solid and was filtered off and vacuum dried (266 mg, 91% yield) (Found: C, 56.2; H, 5.40. Calc. for $C_{49}H_{56}BF_4P_3Pd_2$: C, 56.7; H, 5.44%). IR (Nujol, KBr) 3053m [ν(=C–H)], 1586, 1573m [ν(C=C)] 1054s (br) cm^{-1} [ν(B–F)]. ^{31}P-{^{1}H} NMR [$(CD_3)_2CO$, 298 K]: δ 352.5 (t, $^2J_{PP} = 34$, μ-PBu^t_2), 16.8 (dd, $^2J_{PP} = 34$, $^3J_{PP} = 68$, PPh_3) and 15.8 (dd, $^2J_{PP} = 34$, $^3J_{PP} = 68$ Hz). ^{1}H NMR ($CDCl_3$, 298 K): δ 0.71 (d, $^3J_{HP} = 14.4$, 9 H), 0.825 (d, $^3J_{HP} = 14.3$, 9 H), 0.83 (s, 3 H), 2.35 (dd, $J = 5$, 14.5, 1 H), 2.99 (d, $J = 4$ Hz, 1 H), 3.59 (m, 1 H), 3.74 (m, 1 H), 3.81 (m, 1 H) and 7.50 (m, 30 H).

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