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Review

Chemistry of the phosphinophosphinidene $^tBu_2P$—P, a novel π-electron ligand†‡

Jolanta Olkowska-Oetzel[1] and Jerzy Pikies[2]*

[1]DFG Centre for Functional Nanostructures, Karlsruhe, Germany
[2]Chemical Faculty, Technical University of Gdańsk, Gdańsk, Poland

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In reactions with transition metal compounds, $^tBu_2P$—P=P(X)$^tBu_2$ (X = Br, Me) acts mainly as a precursor of the $^tBu_2P$—P ligand, whereas $^tBu(Me_3Si)P$—P=P(Me)$^tBu_2$ acts as a precursor of the $(Me_3Si)P$=P^tBu ligand. Up to now, only Pt(0) d^{10} ML_2 metal centres were found to be able to stabilize the $^tBu_2P$—P group in 'pure form' by means of η^2-coordination (side on). Several compounds of the $[\{\eta^2-{}^tBu_2P\text{—}P\}Pt(PR_3)_2]$ type were sufficiently stable to be isolated and characterized; however, not all of them gave single crystals suitable for X-ray structure determinations. The X-ray structures of these compounds and of $[\{\mu-(1,2{:}2-\eta-{}^tBu_2P\text{—}P)Pt(PR_3)_2\}\{M(CO)_5\}]$ strongly suggest the ethene-like form of 1,1-di-*tert*-butyldiphosphene in these complexes. Such a form is also in agreement with RI DFT calculations with SVP basis for free $^tBu_2P$—P. However, in trapping experiments with cyclic olefins and cyclic dienes $^tBu_2P$—P exhibits, to some extent, electrophilic 'singlet carbene' properties.

KEYWORDS: phosphinophosphinidenes; diphosphenes; platinum; side-on coordinated transition metal complexes

INTRODUCTION

The aim of this review is to show the chemical properties of the phosphinophosphinidene $^tBu_2P$—P, both in experiments with trapping agents and in experiments with transition metal compounds. We also want to compare these properties with properties of phosphinidene complexes, especially with properties of aminophosphinidenes and their complexes.

Phosphinidenes (R—P)[1,2] and their complexes are known to be important transient species.[3] Theoretical studies have shown that phosphinidenes R—P exhibit an inherent triplet electronic ground state but that the singlet state can be stabilized by substituents.[4] Theoretical investigations at HF and MP2 levels have shown that substituents R acting as π-donors stabilize the singlet state.[5] Thus, for R = PH_2 and NH_2 the phosphinidenes have a closed shell singlet state. Replacing the hydrogen atoms with methyl groups further favours the singlet state because of the inductive effect of the methyl group and because of steric repulsion, which distorts the pyramidal geometry of the triplet state. For Me_2P—P, the triplet–singlet energy gap is about 15.5 kJ mol^{-1}. However, a considerable stability of the singlet state (energy gap of about 34.3 kJ mol^{-1}) was found only for diaminophosphinophosphinidene.[6]

The properties of phosphinidenes as ligands have been intensively studied. The complexes of these species can be divided into two classes:

(1) Electrophilic complexes of general formula [R—P—M], resembling Fischer's carbene complexes, where M is a zero-valent transition metal fragment, mainly $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$ or $Fe(CO)_4$.[2,3] These unstable complexes have a very rich chemistry resembling those of singlet carbenes.[7,8] The most important features are [2 + 1] addition with alkynes and acceptor properties towards Lewis bases. These complexes possess an electrophilic character even in the case of the strong electron-releasing group R = $^iPr_2N$.[9] The M—P bond mainly has the character of a single bond.[10]

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*Correspondence to: J. Pikies, Chemical Faculty, Technical University of Gdańsk, Narutowicza 11–12, 80-952 Gdańsk, Poland.
E-mail: pikies@altis.chem.pg.gda.pl

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(2) Nucleophilic complexes R—P—M, where the metal M is in a high oxidation state. Their reactivity resembles the reactivity of Schrock's carbene complexes.[7] These complexes undergo [2 + 2] cycloaddition reactions with alkynes, as well as addition reactions with Lewis acids, and exhibit often strongly deshielded ^{31}P NMR signals of the phosphinidene phosphorus atoms. The M—P bond possesses the character of a multiple bond.[11] Some of these complexes can be stabilized by sterically demanding R groups.[11–13]

The coordination of phosphinidenes to transition metal fragments has been studied at different levels of theory. In our opinion, the first study of Trinquier and Bertrand[14] (mainly the EHT level) was a very important one. H_2P—P was considered to be in a planar singlet form with a P—P distance of 193 pm. The analysis of the orbital interactions of η^1-coordinated H_2P—P with various ML_n metal fragments suggests that the strongest interactions should be with 14-electron species, such as d^4 ML_5, d^6 ML_4 and d^8 ML_3. Considering some similarities of the molecular orbitals of this ligand to ethene orbitals led the above authors to suggest the possibility of η^2-coordination. The importance of such a coordination was supported by experimental results of the G. Fritz group. *Ab initio* calculations on the parent H_2P—P showed a dissymmetry of the coefficients of both phosphorus atoms in the molecular orbital of b_1 symmetry (π-system), and in our opinion this has a significant impact on the structures of η^2-coordinated complexes of $^tBu_2P$—P.

The coordination of the R—P unit was studied more intensively and at higher levels of theory. It was established that the coordination of the R—P moiety strongly favoured the singlet state of the resulting complex.[4,6] Moreover, it was found (CASPT2 + relativistic correlation and B3LYP) that, in the case of η^1-H_2P—P—$Cr(CO)_5$, the Cr—P bond is mainly a single bond because of the poor availability of empty p-orbitals of the ligating phosphorus atom, due to internal conjugation in the P—PH_2 group.[15] These two papers,[6,15] however, did not consider the possible η^2-coordination of the H_2P—P moiety.

CHEMICAL, STRUCTURAL AND ELECTRONIC PROPERTIES OF THE ^{t}Bu$_2$P—P LIGAND

The phosphinophosphinidenephosphoranes $^tBu_2P$—P=P(X)$^tBu_2$ (X = Br (**1a**), Me (**1b**)) were mainly used as precursors of the unstable $^tBu_2P$—P moiety according to the simplified Eqn. (1):

$$\begin{aligned}&{}^tBu_2P\text{—}P\text{=}P(X){}^tBu_2 \rightarrow\\&[{}^tBu_2P\text{—}P] + {}^tBu_2PX \qquad (X = Br, Me)\end{aligned} \tag{1}$$

So far, we have no proof that $^tBu_2P$—P can exist, not even as a transient species. Attempts to isolate this intermediate in an argon matrix were unsuccessful.[16]

Despite its electron-releasing $^tBu_2P$ group, the hypothetical free $^tBu_2P$—P (from a theoretical point of view) seems to be significantly electrophilic, and this species should possess a singlet ground state. The fairly good stability of $^tBu_2P$—P=P(Br)$^tBu_2$ (**1a**) and $^tBu_2P$—P=P(Me)$^tBu_2$ (**1b**) could support such an assumption. These two compounds can be interpreted as being the result of an addition of a phosphinidene to a Lewis base P(X)$^tBu_2$. The trapping experiments are in agreement with this assumption, and the formation of phosphiranes from **1a** and **1b** in the reactions with cyclic olefins and cyclic dienes[17–19] can be interpreted as being proof of the electrophilic character and the singlet ground state of $^tBu_2P$—P. The nucleophilic properties of **1a** and **1b** towards Lewis acids have not been studied so far.

The reaction of **1a** or **1b** with 2,3-dimethyl-1,3-butadiene differs significantly from the reactions of electrophilic phosphinidene complexes with conjugated dienes. The minor product results from a [2 + 1] addition of $^tBu_2P$—P to a double bond of 2,3-dimethyl-1,3-butadiene, the major product results formally from a Diels–Alder reaction of the phosphinophosphinidene dimer $^tBu_2P$—P=P—P$^tBu_2$ with this diene.[19] The main product in the thermal decomposition of **1a** or **1b** without trapping agents is the cyclic tetramer $P_4(^tBu_2P)_4$, besides bis(di-*tert*-butylphosphino)bicyclo[1.1.0]-tetraphosphane with a butterfly structure and the cyclic trimer $P_3(^tBu_2P)_3$.[19] All reactions of **1a** and **1b** were accompanied by the formation of $^tBu_2PH$, which is probably due to splitting of the P—P bond of the $^tBu_2P$—P moiety, but the reason for this is unknown. The formation of the head-to-tail cyclic dimer $1\lambda^5,3\lambda^5,2\lambda^3,4\lambda^3$-tetraphosphete was not observed. One compound of such a type is known,[20] but no direct evidence for a transient phosphinophosphinidene could be obtained. The thermal decomposition reactions of electrophilic phosphinidene complexes yield head-to-head dimers.[3] Precursors **1a** and **1b** did not give rise to any insertions into the Si—H bond of Et_3Si—H and they did not react with Ph_2CO.[21]

An attempt to generate transient $^tBu_2P$—P via UV photolysis (λ >320 nm) of **1b** resulted in the formation of a planar *iso*tetraphosphane $(^tBu_2P)_3P$ together with $^tBu_2PH$, $^tBu_2P$—P$^tBu_2$, $^tBu_2P$—P^tBu(H) and yellow polymers.[21,22]

The transient phosphonitrenes RR′P—N tend to polymerize via head-to-tail addition, yielding cyclodiphosphazenes, cyclotriphosphazenes and polyphosphazenes.[23]

The electronic structure of the $^tBu_2P$—P ligand was investigated at various levels of theory[24] (see also Ref. 21):

(1) *Ab initio* calculations with STO-3G basis (Hartree–Fock approximation) show a pyramidal molecule with a relatively short (206.6 pm) and polarized $^tBuP^{(+0.24)}$—$P^{(-0.03)}$ P—P bond. The partial charges at the phosphorus atoms are estimated according to a Millikan population analysis.

(2) *Ab initio* calculations with 3-21G basis (Hartree–Fock

approximation) lead to a planar molecule with a relatively short (205.2 pm) and polarized $^tBu_2P^{(+0.47)}$—$P^{(-0.06)}$ P—P bond.

(3) The RI DFT method of the TURBOMOLE package[25,26] with SVP basis indicates a planar molecule with a short (197.1 pm) and polarized $^tBu_2P^{(+0.18)}$—$P^{(-0.18)}$ P—P bond. These results seem to be the most reliable ones, and they indicate a P—P bond distance that is comparable to data obtained from *ab initio* calculations for Me_2P—P at a very high level of theory (QCISD(T)/ 6-311 ++ G(3df,2p) + ZPE basis) showing a planar molecule with a short (194.5 pm) bond.[5] Similar results for H_2P—P (196.3 pm) were obtained applying the B3LYP method.[15]

The results presented clearly indicate that $^tBu_2P$—P has a short P—P bond, shorter than a double P=P bond in diphosphenes (~204 pm),[27] and that it has a significant ionicity.

THE REACTIONS OF ^{t}Bu$_2$P—P=P(X)^{t}Bu$_2$ (X = Br, Me) WITH TRANSITION METAL COMPLEXES

The cluster complex $[\{(P_3C_5{}^tBu_5)P2—P1\}\{Ru_3(CO)_9\}]$[28] was the first complex found containing a phosphinophosphinidene $(P_3C_5{}^tBu_3)P2—P1$ moiety. Its structure can be rationalized in terms of η^2-coordination of a multiple P1—P2 bond (216.4 pm) to an $Ru(CO)_3$ group. The terminal P1 atom acts additionally as a μ_2 ($4e^-$) donor towards the $Ru_2(CO)_6$ fragment. The phosphidophosphinidene cluster $[Ta(P_3C_2{}^tBu_2)_3(\mu_3\text{-}P_4)(\mu_3\text{-}P_2)Fe(CO)_4]$ exhibits a very short P—P bond (208.8 pm).[29] All other phosphinophosphinidene complexes were obtained by the G. Fritz group.[30] With regard to the products, the reactions of $^tBu_2P$—P=P(Br)$^tBu_2$ (**1a**) and $^tBu_2P$—P=P(Me)$^tBu_2$ (**1b**) with transition metal complexes can be attributed to the four reaction types discussed below.

Reactions of ^{t}Bu$_2$P—P=P(X)^{t}Bu$_2$ (1, X = Me, Br) with transition metal compounds without splitting of the ^{t}Bu$_2$P—P bond

$^tBu_2P$—P=P(Me)$^tBu_2$ (**1b**) reacts with $[(\eta^2\text{-}C_2H_4)Pt(PR_3)_2]$ according to Eqn. (2), yielding $[(\eta^2\text{-}{}^tBu_2P—P)Pt(PR_3)_2]$ (**2**), which contains $^tBu_2P$—P as an η^2-coordinated ligand.[31–34] The reactions take place below the temperature of thermal decomposition of **1b**; they should be regarded, rather, as reactions of precursor **1b**, but not of the transient $^tBu_2P$—P with $[(\eta^2\text{-}C_2H_4)Pt(PR_3)_2]$.

$$\begin{aligned}&{}^tBu_2P—P{=}P(Me)^tBu_2 + [(\eta^2\text{-}C_2H_4)Pt(PR_3)_2] \rightarrow\\&[(\eta^2\text{-}{}^tBu_2P—P)Pt(PR_3)_2] + {}^tBu_2PMe + C_2H_4\end{aligned} \quad (2)$$

X-ray structure determinations of **2a** $(PR_3)_2 = (PPh_2Et)_2$,[31] **2b** $(PR_3)_2 = PPh_3$, P^tBu_2H,[33] and **2c** $(PR_3)_2$ = dppe[34] reveal that the four phosphorus atoms and the platinum atom are almost in one plane. The η^2-coordination of $^tBu_2P$—P to the $Pt(PR_3)_2$ moiety forms a characteristic triangle, e.g. **2a**,[31] with a very short $^tBu_2P$—P bond (207.1 pm), a long $^tBu_2P$—Pt bond (231.3 pm) and a very long P—Pt bond (238.8 pm). The bond distances correlate well with the ^{31}P NMR data: $^1J(^tBu_2P—P) = -611.7$ Hz, $^1J(Pt—{}^tBu_2P) = 1900$ Hz, $^1J(Pt—P) = -78.4$ Hz. This impressive molecular geometry can be rationalized in terms of a dissymmetry[14,24] of the coefficients of the phosphorus atoms in the $^tBu_2P$—P π molecular orbitals of the $^tBu_2P$—P group. Taking into account the multiple bond elongation due to the side-on coordination, the short $^tBu_2P$—P distance correlates very well with the value obtained by the RI DFT method.[24] The steric constitution of this ligand (^tBu—P—^tBu part) is very similar to that of an η^2-coordinated ethene (H—C—H part) linked to a d^{10} ML_2 metal centre. Thus, complex **2** is better represented by the ethene-like species **A** with a short P—P double bond and significant ionicity, rather than by a compound of type **B** (Fig. 1). Small and strong σ-donating phosphines R_3P increase the thermal stability of complexes **2**.[32] It is not possible to remove the $^tBu_2P$—P unit from the Pt(0) centre in **2** by an attack of bidentate chelate ligands, e.g. by dppe ($Ph_2PCH_2CH_2PPh_2$). In this case the two R_3P groups but not the $^tBu_2P$—P moiety were replaced by dppe.[34]

Figure 1. Possible structures of complex **2**.

The other d^{10} ML_2 metal centres (M = Ni, Pd) form compounds with ^{31}P NMR spectra similar to complexes **2**. However, we were not able to isolate them as single crystals.

Treatment of **2** with $^tBu_2P$—P=P(Me)$^tBu_2$ (**1b**) yields the corresponding diphosphene complex $[(2,3\text{-}\eta\text{-}{}^tBu_2P—P{=}P—P^tBu_2)Pt(PR_3)_2]$ (**3**) according to Eqn. (3).[35] The rates and yields of this reaction depend substantially upon the PR_3 groups. The small and strong σ-donating phosphines R_3P favour this reaction. Thus, it seems very likely that the nucleophilicity of the phosphinidene phosphorus atom of **2** plays an important role in this reaction. The X-ray structures of **3a** ($PR_3 = PPh_3$) and **3b** ($PR_3 = PPh_2Et$), and also the NMR data, are in agreement with this formula, i.e. a $^tBu_2P$—P bond distance of 222.4 pm and a P—P bond distance of 215.2 pm for **3a**.

$$\begin{aligned}&{}^tBu_2P—P{=}P(Me)^tBu_2 + [(\eta^2\text{-}{}^tBu_2P—P)Pt(PR_3)_2] \rightarrow\\&[(2,3\text{-}\eta\text{-}{}^tBu_2P—P{=}P—P^tBu_2)Pt(PR_3)_2] + {}^tBu_2PMe\end{aligned} \quad (3)$$

The formation of $1\lambda^5,3\lambda^5,2\lambda^3,4\lambda^3$-tetraphosphete (head-to-tail dimerization) or its complexes was not observed.

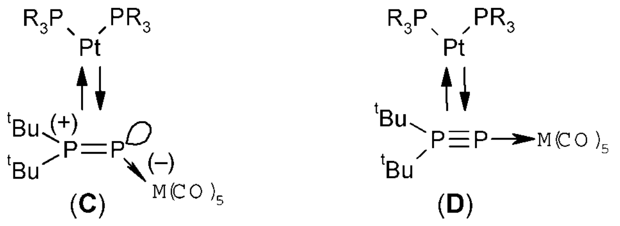


Figure 2. Possible structures of complex **4**.

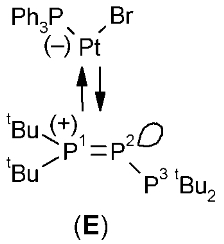


Figure 3. Possible Lewis structure of complex **5**.

By reacting **2** with $[(CO)_5M\cdot THF]$ (M = Cr, W) the corresponding complexes $[\mu\text{-}(1,2{:}2\text{-}\eta\text{-}{}^tBu_2P—P)\{Pt(PR_3)_2\}\{M(CO)_5\}]$ (**4**) are formed (Fig. 2).[36] The X-ray structure determinations of **4a** (R = Ph, M = W) and **4b** (R = $\frac{1}{2}$ dppe, M = Cr) confirm that introducing M(CO)$_5$ (isolobal with singlet carbene) does not change the main structural features of the parent complexes **2**. For **4a**, the following distances were found: ^{t}Bu$_2$P—P 208.8 pm, Pt—P^{t}Bu$_2$ 232.9 pm, Pt—P 238.1 pm, P—W 260.9 pm; for **4b**: P—Cr 247.5 pm. The ^{t}Bu—P bonds and the P—M(CO)$_5$ bond of the ^{t}Bu$_2$P=P—M(CO)$_5$ moiety are considerably bent out of the plane perpendicular to the main plane (defined by the four phosphorus atoms and the platinum atom). The steric effect of an inert electron pair is visible. The P—W bond of **4a** is very long, being 8.8 pm longer than the P—W bond of [Pd{(PhP=PPh)[W(CO)$_5$]$_2$}(dppe)] (252.1 pm).[37] The P—Cr and ^{t}Bu$_2$P—P bonds in **4b** are significantly longer than predicted for the ground state of a singlet (η^1-H$_2$P—P)Cr(CO)$_5$ (P—Cr 235.5 pm, P—P 203.4 pm) but are close to the values for the first excited singlet state of this compound.[15] The elongation of the ^{t}Bu$_2$P—P and P—Cr(CO)$_5$ bonds in **4b** is probably due to back donation from (PR$_3$)$_2$Pt into the lowest unoccupied molecular orbital (LUMO) of ^{t}Bu$_2$P—P—Cr(CO)$_5$. The LUMO of Cr(CO)$_5$—P—PH$_2$ is antibonding between P—P and P—Cr.[15] Thus, the (CO)$_5$M—P bond is a weak donor–acceptor single bond and no dative π-bonding (CO)$_5$M → P is visible. ^1J(P—W) of **4a** (58 or 114 Hz) is in agreement with the character of this bond. This value is even smaller than that reported for [η^1-{(Me$_3$Si)P=C(NMe$_2$)$_2$}W(CO)$_5$] of 143.7 Hz.[38]

Hence, the structural features of **4** can better be assigned to an alkene-type complex **C** rather than to a 1,1-di-*tert*-butyldiphosphyne derivative **D**.

The reaction of ^{t}Bu$_2$P—P=P(Br)^{t}Bu$_2$ (**1a**) with [(η^2-C$_2$H$_4$)Pt(PPh$_3$)$_2$] according to Eqn. (4) yields [(1,2-η-^{t}Bu$_2$P=P—P^{t}Bu$_2$)Pt(PPh$_3$)Br] (**5**).[39] Only one isomer of **5** was found.

$$\begin{aligned}&{}^tBu_2P—P{=}P(Br){}^tBu_2 + [(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2] \rightarrow\\&[(1,2\text{-}\eta\text{-}{}^tBu_2P{=}P—P{}^tBu_2)Pt(PPh_3)Br] + \qquad (4)\\&PPh_3 + {}^tBu_2PMe + C_2H_4\end{aligned}$$

5 exhibits a very short P^1—Pt bond (223.1 pm), a long P^2—Pt bond (240.5 pm) and a short P^1—P^2 bond (214.9 pm), typical for a P—P bond of an η^2-coordinated diphosphene ligand. The P^2—P^3 bond has single bond character (223.7 pm). However, this formal Pt(II) d^8 complex exhibits the typical features of d^{10} ML$_2$ ethene complexes, especially the planar alignment around the platinum atom and the steric alignment of the P^2—P^3 bond like a C—H bond of (PR$_3$)$_2$Pt(η^2-C$_2$H$_4$). The steric effect of an electron-inert pair is visible. The Lewis structure **E** (Fig. 3) can explain the main structural features of **5**, especially the short ^{1}Bu$_2$P—Pt distance and the longer P^1—P^2 distance compared with **2**.

1b reacts with [Mo(CO)$_2$cp^t]$_2$ yielding [μ-(1,2:2-η-^{t}Bu$_2$P—P){Mo(CO)$_2$cp^t}$_2$] (**6**) (cp^t = C$_5$H$_4$^{t}Bu).[40] Despite the fact that **6** (**F**, Fig. 4) seems to be quite similar to **4**, there are some important differences. The steric alignment of ^{t}Bu$_2$P—P—Mo^1 (^{t}Bu$_2$P—Mo^1, 250.6 pm; P—Mo^1, 242.6 pm) is quite different from ^{t}Bu$_2$P—P—Pt in **2**. The terminal bond P—Mo^2 is almost in the plane defined by the central molybdenum atom and the two phosphorus atoms. Taking into account the P—Mo^2 distance (225.9 pm) and the chemical shift of phosphorus (^{31}P NMR, 346.3 ppm), it seems likely that this bond has more than double bond character. Thus, there is no steric effect of an inert electron pair. The ^{t}Bu$_2$P—P bond is very short (211.4 pm). In this compound, ^{t}Bu$_2$P—P acts probably as a 2·3 e$^-$ donor ligand (Fig. 4).

All products of reactions, where there is no P—P splitting in the ^{t}Bu$_2$P—P group and oligomerization does not occur, contain this ligand as an η^2-coordinated unit. Some observations from ^{31}P NMR could be interpreted in terms of terminal bonding of ^{t}Bu$_2$P—P to Fe(0) metal centres, but, up to now, no phosphinophosphinidene complex with the

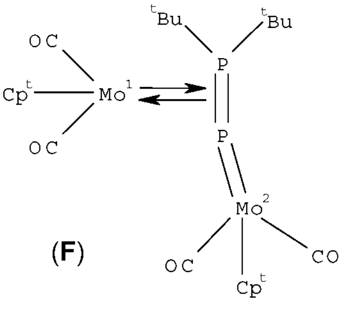


Figure 4. Structure of complex **6**.

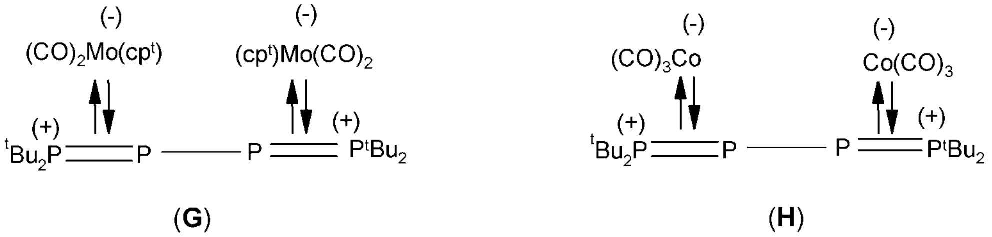


Figure 5. Lewis structures for complexes **7** and **8** (**G** and **H** respectively).

${}^{t}Bu_2P$—P group acting solely as a terminal η^1-ligand has been isolated.

Oligomerization reactions of the ${}^{t}Bu_2P$—P ligand in the coordination sphere of transition metal compounds

Almost all reactions of ${}^{t}Bu_2P$—P=P(X)${}^{t}Bu_2$ (**1**; X = Me, Br) with transition metal compounds are accompanied by some formation of nearly insoluble polymeric species with unknown structures, whereas the ${}^{t}Bu_2P$—P moiety shows a tendency to polymerize in the coordination sphere of transition metals. The extent of this side reaction depends on the ability of the metal to serve better or poorer as a coordination centre, and on the stability of the primary products formed. Such low molecular weight compounds lead to isolable products only in a few cases.

Up to now, we have obtained only head-to-head products from dimerizations or trimerizations of the ${}^{t}Bu_2P$—P moiety in the coordination sphere of the transition metal compounds investigated. As an example, the formation of [(2,3-η-${}^{t}Bu_2P$—P=P—P${}^{t}Bu_2$)Pt(PR_3)$_2$] (**3**) has already been mentioned.[35]

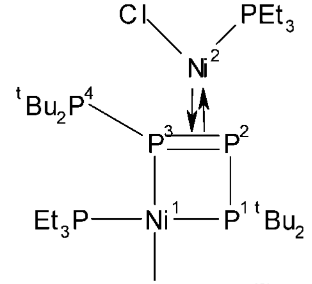
Compound **1b** reacting with [Mo(CO)$_2$cp^t]$_2$ yields the dinuclear complex [μ-(1,2:3,4-η-${}^{t}Bu_2P$=P—P=P${}^{t}Bu_2$) {Mo(CO)$_2$cp^t}$_2$] (**7**) in addition to **6**.[41] The P—P distance is about 222 pm; the ${}^{t}Bu_2P$—P bonds are substantially shorter (~211 pm). X-ray structure determination of **7** suggests that ${}^{t}Bu_2P$—P contains an η^2-coordinated double bond linked to Mo(I), which has to be considered as a formal d^5, but more probably as a d^6, metal centre.

Similar products, diastereomeres of [μ-(1,2:3,4-η-${}^{t}Bu_2P$=P—P=P${}^{t}Bu_2$) {Co(CO)$_3$}$_2$] (**8**), are formed in the reaction of **1b** with [$Co_2(CO)_8$].[42] These interesting compounds exhibit short ${}^{t}Bu_2P$—P distances (~213 pm), whereas the P—P distance (222 pm) is in the typical P—P single bond range. The ${}^{t}Bu_2P$—Co distance (218.2 pm) is substantially shorter than the P—Co distance (235.1 pm). Thus, ${}^{t}Bu_2P$—P contains an η^2-coordinated double bond bonded to Co(0), which has to be considered as a formal d^9, but more probably as a Co(−I) d^{10}, metal centre. The Lewis structures **G** and **H** clearly explain the main structural features of **7** and **8** respectively (Fig. 5).

${}^{t}Bu_2P$—P=P(Me)${}^{t}Bu_2$ (**1b**) reacts with [$(Et_3P)_2NiCl_2$] and naphthyl—Na to yield, among other things, the dinuclear complex [μ-(1,3:2,3-η-${}^{t}Bu_2P$—P=P—P${}^{t}Bu_2$) {NiCl(PEt_3)}$_2$] (**9**) (**I**, Fig. 6).[43] The P^2—P^3 bond (216.1 pm) of **9** can be characterized as an η^2-coordinated double bond. However, with [$(Et_3P)_2NiCl_2$] and Na/Hg, **1b** yields the complex [(2,3-η-${}^{t}Bu_2P$—P=P—P${}^{t}Bu_2$)Ni(PEt_3)$_2$] (**10**), similar to **3**, which has so far only been characterized by ${}^{31}P$ NMR spectra.[35,43]

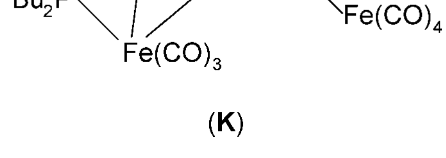
The reaction of **1b** with [$Fe_2(CO)_9$] yields, among other things, [μ-(1,2,3:4-η-${}^{t}Bu_2$PPPP${}^{t}Bu_2$) {Fe(CO)$_3$} {Fe(CO)$_4$}] (**11**). Similarly, **1b** with [Fe(CO)$_3$(η^2-C_8H_{14})$_2$] yields [μ-(1,2,3:4-η-${}^{t}Bu_2$PPPP${}^{t}Bu_2$) {Fe(CO)$_3$} {Fe(CO)$_3$(${}^{t}Bu_2$PMe)}].[44] The remarkable structural feature of **11** is the presence of a ${}^{t}Bu_2$PPPP${}^{t}Bu_2$ moiety and its 1,2,3-η^3-coordination to a 14e$^-$ Fe(CO)$_3$ centre. The bond distances P^1—P^2 (214.6 pm) and P^2—P^3 (213.9 pm) are typical for side-on bonded P=P double bonds. The P^3—P^4 bond (223.9 pm) has a single bond character (**K**, Fig. 7).

There are significant differences between the reactivity of ${}^{t}Bu_2P$—P and R_2N—P moieties. A tendency of R_2N—P to act



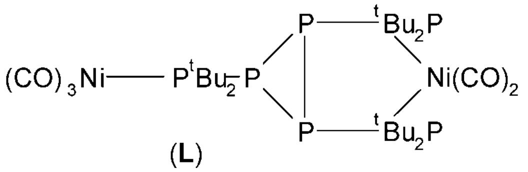
(I)

Figure 6. Structure of complex **9**.



(K)

Figure 7. Structure of complex **11**.



(**L**)

Figure 8. Structure of the dinuclear model complex **12**.

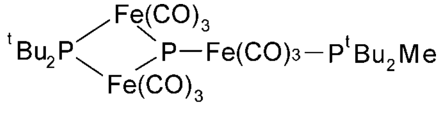
as a terminal ligand is obvious.[10] R_2N—P dimerizes head-to-head to yield an η^2-diphosphene complex with an $Fe(CO)_4$ centre, but η^3-coordination was not observed.[45] $^iPr_2N$—PCl_2 with $Na_2[Fe(CO)_4]$ yields mainly the carbonyl-bridged phosphorus derivative $[\{(^iPr_2NP)_2CO\}Fe_2(CO)_6]$ or the triphosphane (but not cyclotriphosphane) derivative $[(^iPr_2NP)_3Fe_2(CO)_6]$.[45–47] η^2-Bonding of R_2N—P was not observed.

The reaction of $^tBu_2P$—P=P(X)$^tBu_2$ (**1**) with an excess of $[Ni(CO)_4]$ yields the dinuclear nickel complex [{*cyclo*-$P_3(P^tBu_2)_3$} {$Ni(CO)_2$} {$Ni(CO)_3$}] (**12**) centred around a trimer of $^tBu_2P$—P (**L**, Fig. 8).[48] With a 1:1 ratio of **1b** to $[Ni(CO)_4]$ the related mononuclear [{*cyclo*-$P_3(P^tBu_2)_3$} {$Ni(CO)_2$}] was formed. The $Ni(CO)_n$ groups ($n = 2$ or 3) obviously are not able to stabilize the $^tBu_2P$—P monomer sufficiently, probably because of the greater π-acidity of the CO ligand compared with the PR_3 groups. In this reaction we did not observe either the formation of *cyclo*-$P_4(^tBu_2P)_4$ or of its complexes with $Ni(CO)_n$ centres; however, in the thermal decomposition of **1**, this tetramer is the main product.[19] The related complex [{*cyclo*-$P_4(^tBu_2P)_4$} $\{Ni(CO)_2\}_2$] (independently obtained[49]), showed low thermal stability.

Reactions of $^tBu_2P$—P=P(Me)$^tBu_2$ (1b) with transition metal compounds via cleavage of the $^tBu_2P$—P bond

$^tBu_2P$—P=P(Me)$^tBu_2$ (**1b**) reacts with $[Co_2(CO)_8]$ to yield $[Co_4P_2(P^tBu_2)_2(CO)_8]$ (**13**) in addition to **7**.[42] X-ray structure determination shows that the cluster **13** has a tetragonal bipyramidal structure with four cobalt atoms in the basal plane and two phosphorus atoms in the apical positions. Two bridging μ_2-P^tBu_2 groups are also situated in the basal plane.

Among several other products, the reaction of **1b** with $[Fe(CO)_3(\eta^2\text{-}C_8H_{14})_2]$ yields the unexpected complex [(μ-$^tBu_2P$) {μ-P—$Fe(CO)_3$—P^tBu_2Me} $\{Fe(CO)_3\}_2$](P—P) (**14**),[44] in which $Fe(CO)_3$ groups formally seem to be inserted into each P—P bond of **1b** (**M**, Fig. 9). **1b** reacts with $(Et_3P)_2PdCl_2$ and naphthyl—Na to yield, among other things, the dinuclear complex [μ-$^tBu_2P$—$Pd(PEt_3)]_2$(Pd—Pd).[50]



(**M**)

Figure 9. Structure of complex **14**.

Other unusual reactions of $^tBu_2P$—P=P(Me)$^tBu_2$ and $^tBu(Me_3Si)P$—P=P(Me)$^tBu_2$ with transition metal compounds

1b reacts with $[(\eta^2\text{-}C_2H_4)_2Co(cp^*)]$ to yield [(1,2,3-η-$^tBu_2P$—P=$CHCH_3$)Co(cp*)] (**15**) (cp* = C_5Me_5) according to Eqn. (5):[51]

$$[cp^*Co(\eta^2\text{-}C_2H_4)_2] + {}^tBu_2P\text{—}P{=}P(Me)^tBu_2 \rightarrow [(1,2,3\text{-}\eta\text{-}^tBu_2P\text{—}P{=}CHCH_3)Co(cp^*)] + C_2H_4 + {}^tBu_2PMe \quad (5)$$

The formation of the η^3-coordinated ligand $^tBu_2P$—P=$CHCH_3$ is due to the reaction of $^tBu_2P$—P with one of the C_2H_4 molecules (1,2 hydrogen shift within this molecule) in the coordination sphere of the $14e^-$ Co(I) metal centre. The $^tBu_2P$—P bond (215.6 pm) has to be considered as a side-on coordinated P=P double bond.

The reaction of $^tBu(Me_3Si)P$—P=P(Me)$^tBu_2$ (**1c**) with $[(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2]$ yields a Pt(0) complex of a diphosphene, $[(\eta^2\text{-}Me_3SiP{=}P^tBu)Pt(PPh_3)_2]$ (**16**; Eqn. (6)):

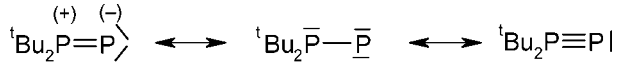
$$^tBu(Me_3Si)P\text{—}P{=}P(Me)^tBu_2 + [(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2] \rightarrow [(\eta^2\text{-}Me_3SiP{=}P^tBu)Pt(PPh_3)_2] + C_2H_4 + {}^tBu_2PMe \quad (6)$$

In this reaction the Me_3Si group undergoes a 1,2 shift within the $^tBu(Me_3Si)P$—P ligand. We could not detect any traces of the expected product $[\{\eta^2\text{-}^tBu(Me_3Si)P\text{—}P\}Pt(PPh_3)_2]$.[52] Nevertheless, $^tBu(Me_3Si)P$—P=P(Me)$^tBu_2$ reacts with PEt_3 to yield $^tBu(Me_3Si)P$—P=PEt_3, and no parallel 1,2 shift of the Me_3Si group occurs.[53]

CONCLUSION

$^tBu_2P$—P can be considered in terms of the three possible canonical forms, **N**, **O** and **P**, shown in Fig. 10. There are no experimental data regarding the free $^tBu_2P$—P. Theoretical investigations (very short P—P bond distance and planar molecular structure) suggest that form **N** seems to be the best illustration of the electronic structure of the free $^tBu_2P$—P group.

The reaction of $^tBu_2P$—P=P(Me)$^tBu_2$ with Pt(0) complexes to yield $(\eta^2\text{-}^tBu_2P\text{—}P)Pt(PR_3)_2$ (**A**, Fig. 1) also indicates that this reaction strongly stabilizes the form **N**, but so far it has only been possible to isolate the η^2-complexes of $^tBu_2P$—P in a 'pure form' for the Pt(0) d^{10} ML_2 centre. The most striking



(**N**) (**O**) (**P**)

Figure 10. Three possible canonical forms of $^tBu_2P$—P.

property, different from the behaviour of $R_2N—P$, is a strong tendency to side-on coordination. Such a coordination seems to be essential to stabilize this ligand, and all recently isolated compounds containing $^tBu_2P—P$ show η^2-coordination.

On the other hand, the reactions of $^tBu_2P—P{=}P(X)^tBu_2$ (**1**; X = Me, Br) with cycloalkenes to yield phosphiranes, as well as the trimerization and tetramerization of the $^tBu_2P—P$ moiety in the thermal rearrangement of **1**, suggest a singlet ground state and electrophilic properties of the hypothetical free phosphinophosphinidene $^tBu_2P—P$ in these types of reaction. Thus, its reactivity can be attributed to form **O**.

The X-ray structures of complex compounds with the $^tBu_2P—P$ ligand show no indications for any contribution of the form **P**.

However, one must consider that all our conclusions regarding the chemical properties of $R_2P—P$ and its complexes were based on reactions involving mainly $^tBu_2P—P$ ligands and only in one case the $^tBu(SiMe_3)P—P$ ligand. The R groups were sterically demanding and had electron-donating character. Investigations in the synthesis of new precursors and their reactions are currently in progress.

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