

Reactivity of Carbonyl-Functionalized Phosphaalkenes $\text{RC}(\text{O})\text{P}=\text{C}(\text{NMe}_2)_2$ ($\text{R} = t\text{Bu}, \text{Ph}$) towards Electrophiles

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Dedicated to Professor Dirk Walther on the occasion of his 60th birthday

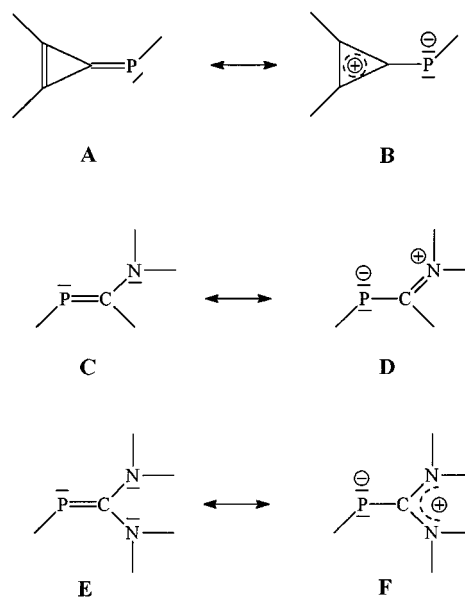
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The reaction of the carbonyl-functionalized phosphaalkenes $\text{RC}(\text{O})\text{P}=\text{C}(\text{NMe}_2)_2$ [$\text{R} = t\text{Bu}$ (**2a**), Ph (**2b**)] with protic acids and alkylating reagents occurred at the two-coordinate phosphorus atom to give the phosphanyl-substituted carbocations **3a,b** and **4a,b**. In contrast, treatment with $\text{Me}_3\text{SiOSO}_2\text{CF}_3$ resulted in attack at the oxygen atom by the silyl group, and the formation of $[\text{RC}(\text{OSiMe}_3)=\text{PC}(\text{NMe}_2)_2]\text{SO}_3\text{CF}_3$ (**5a,b**). Similarly, the Lewis acids $\text{B}(\text{C}_6\text{F}_5)_3$, $\text{Al}(t\text{Bu})_2\text{Cl}$ and AlMe_3 were ligated to the oxygen atom of the carbonyl group. Two equivalents of GaMe_3 were added to the oxygen and phosphorus atom of the phosphaalkene to yield the thermolabile complexes

$[\text{RC}(\text{OGaMe}_3)=\text{P}(\text{GaMe}_3)\text{C}(\text{NMe}_2)_2]$ (**10a,b**). In contrast, one molecule of InMe_3 was bound to the phosphorus center of the phosphorus compound. Reaction of the phosphaalkenes with $[\text{Ni}(\text{CO})_4]$, $[\text{Fe}_2(\text{CO})_9]$ or $[\{(\text{Z})\text{-cyclooctene}\}\text{Cr}(\text{CO})_5]$ also took place at the pnictogen atom, resulting in complexes of the type $[\text{RC}(\text{O})\text{P}\{\text{M}(\text{CO})_n\}\text{C}(\text{NMe}_2)_2]$ ($\text{R} = t\text{Bu}, \text{Ph}$; $\text{M} = \text{Ni}$, $n = 3$; Fe , $n = 4$; Cr , $n = 5$). The chemical transformations reported here underline the versatile chemistry of phosphaalkenes and emphasize a relationship between carbonyl-functionalized phosphaalkenes and the well-investigated class of phosphorus ylides. X-ray structures of compounds **6b**, **7b***, **10a**, **11a** and **12a** are reported.

Introduction

The chemistry of low-coordination phosphorus compounds is a rapidly expanding field that highlights the remarkable ability of phosphorus to mimic the chemistry of carbon.^[1] In the vast majority of phosphaalkenes $\text{R}^1\text{P}=\text{CR}^2\text{R}^3$ and phosphaalkynes $\text{RC}\equiv\text{P}$, the multiple bonds are polarized in the sense $\text{P}^{\delta+}\cdots\text{C}^{\delta-}$, as anticipated by the different electronegativities of phosphorus and carbon. It was pointed out by Regitz et al. that in phosphatriafulvenes **A** (Scheme 1) the $\text{P}=\text{C}$ bond has an inverse electron density;^[2] this was substantiated by quantum chemical calculations in comparison to the parent compound $\text{HP}=\text{CH}_2$. The latter molecule has a $\sigma + \pi$ Mulliken charge distribution of $+0.154$ electrons at the phosphorus and -0.564 electrons at the carbon atom, whereas the PC π -bond is essentially nonpolar ($+0.021 \text{ e}^-$ at P ; 0.021 e^- at C). In the cyclopropylidene phosphane **A** a $\sigma + \pi$ Mulliken charge distribution of -0.037 e^- at the phosphorus and of -0.177 e^- at the carbon atom of the exocyclic double bond were calculated. Here the PC π -bond is clearly polarized towards the phosphorus atom as the negative end of the dipole with an excess of 0.369 e^- at the P atom and a deficiency of 0.084 e^- at the C -atom. The positive charge is stabilized by incorpor-

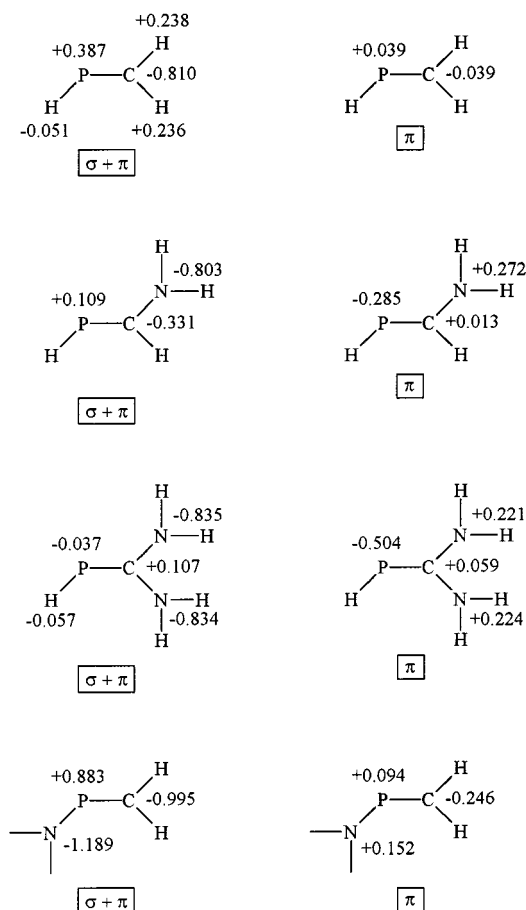


ation into the Hückel aromatic cyclopropenium unit (formula **B** in Scheme 1).

Grobe et al. discovered that the introduction of one dialkylamino group at the carbon atom of the double bond in molecules such as $\text{F}_3\text{CP}=\text{C}(\text{F})\text{NR}_2$ also resulted in an inverse electron distribution of the $\text{P}=\text{C}$ π -bond.^[3] In order to uncover the role of an amino group on the electron distribution in a phosphaalkene we performed quantum chemical calculations at a density functional level [B3LYP/6-31 g(d)].^[4a-4e]

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Scheme 2. Charge distribution in $\text{HP}=\text{CH}_2$ and amino-substituted phosphalkenes

As has been found previously^[2] the calculations predict that the parent phosphalkene should have a nonpolar π -bond (NBO charges and populations),^[4d] although one amino group or, to a greater extent, two amino groups at the carbon atom^[5] induce an inverse electron-density distribution at the π -bond, i.e. the charge at the phosphorus is increased relative to the parent methylenephosphane. Alternatively, an amino group at the phosphorus does the opposite, it enhances π -electron density at the carbon atom. Phosphalkenes with an inverse electron density exhibit peculiarities in their coordination behavior towards 18 VE transition metal fragments. In η^1 -complexes of normally polarized phosphalkenes ($\text{P}^{\delta+}=\text{C}^{\delta-}$) such as $[(\text{MesP}=\text{CPh}_2)\text{Cr}(\text{CO})_5]$ a trigonal planar phosphorus atom is linked to the methylene carbon atom by a $\text{P}=\text{C}$ double bond of 1.679(4) Å.^[6a] In the complex $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{-FeP}[\text{Cr}(\text{CO})_5]\text{C}(\text{NMe}_2)_2]$, however, where the inversely polarized phosphalkene $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeP}=\text{C}(\text{NMe}_2)_2]$ is η^1 -ligated to the $[\text{Cr}(\text{CO})_5]$ group, a trigonal-pyramidal phosphorus atom (sum of angles 346.1°) forms a single bond of 1.793(5) Å to the planar carbon atom.^[7] For comparison, in the free phosphalkene a $\text{P}=\text{C}$ double bond of 1.709(5) Å was measured.^[7c] Obviously the zwitterionic structures of inversely polarized phosphalkenes are stabilized by ligation to metal centers.

In the $\text{W}(\text{CO})_5$ complex of the inversely polarized phosphatrimethylphosphine $\text{MesP}=\text{C}^a\text{C}^b(\text{tBu})-\text{C}^c\text{tBu}(\text{C}^a-\text{C}^c)$, however, the PC double bond [1.679(5) Å] is retained, and the phosphorus atom is pyramidalized to a lesser extent (sum of angles 352.9°).^[2b]

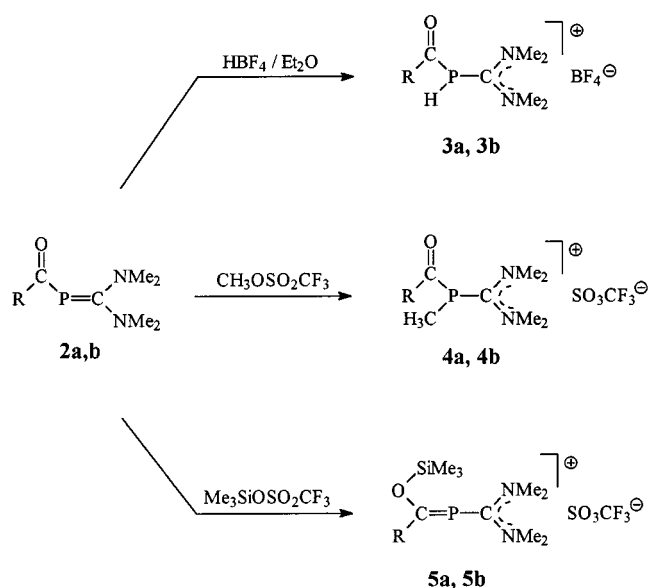
From carbanion and ylide chemistry^[8] it is well documented that the negative charge on a carbon center is effectively stabilized by adjacent carbonyl groups via π -delocalization. In keeping with this, stabilization of the negative charge on the P-atom in phosphatrimethylphosphines^[2b] and amino-functionalized phosphalkenes has been achieved by acyl, dithiocarboxy, and thiocarbamoyl groups.^[9] A significant charge transfer from phosphorus to the acyl-substituents was documented in the IR spectra, where the $\nu(\text{CO})$ bands exhibited marked shifts to lower wavenumbers. Thus, in the IR spectrum of $\text{RC}(\text{O})\text{P}=\text{C}(\text{NMe}_2)_2$, $\nu(\text{CO})$ bands at 1563 cm^{-1} ($\text{R} = \text{tBu}$) and 1546 cm^{-1} ($\text{R} = \text{Ph}$) are found;^[9] the IR spectrum of the “normally polarized” phosphalkene $\text{tBuC}(\text{O})\text{P}=\text{C}(\text{OSiMe}_3)(\text{tBu})$ shows a $\nu(\text{CO})$ band at 1664 cm^{-1} ,^[10] which is well within the range of $\tilde{\nu} = 1630\text{--}1690$ cm^{-1} usually encountered in acyl phosphanes.^[11] Although a number of P-acyl phosphalkenes with an inverse electron density have been prepared, information on the chemistry of these molecules is scarce. Thus, only dimerization and isomerization processes of several phosphatrimethylphosphines, as well as the formation of the complex $[\text{tBuC}(\text{O})\text{P}\{\text{W}(\text{CO})_5\}=\text{C}^a-\text{C}^b(\text{tBu})=\text{C}^c\text{tBu}](\text{C}^a-\text{C}^c)$ have been investigated.^[2b]

We decided to study in more detail the chemical reactivity of $\text{tBuC}(\text{O})\text{P}=\text{C}(\text{NMe}_2)_2$ (**2a**) and $\text{PhC}(\text{O})\text{P}=\text{C}(\text{NMe}_2)_2$ (**2b**), which are readily available from $\text{Me}_3\text{SiP}=\text{C}(\text{NMe}_2)_2$ (**1**) and carboxylic acid chlorides, especially with respect to the related carbonyl-stabilized phosphorus ylides $\text{RC}(\text{O})\text{CH}=\text{PPh}_3$. Here we report on the reactions of **2a** and **2b** with protic acids, alkylating and silylating reagents, organometallic compounds of group 13 elements, and transition metal carbonyl complexes.

Results and Discussion

Reaction of **2a,b** With Protic Acids, ROSO_2CF_3 ($\text{R} = \text{Me}$, SiMe_3) and $\text{B}(\text{C}_6\text{F}_5)_3$

The reaction of the P-acyl phosphalkenes **2a** and **2b** with equimolar amounts of ethereal HBF_4 in diethyl ether at -50°C led to the formation of the phosphanyl carbenium salts $[\text{RC}(\text{O})\text{P}(\text{H})\text{C}(\text{NMe}_2)_2][\text{BF}_4]$ **3a** ($\text{R} = \text{tBu}$) and **3b** (Ph) (Scheme 3). Salt **3a** was obtained as a colorless solid and **3b** as a yellow viscous oil. Both compounds are highly soluble in CH_2Cl_2 and CHCl_3 . In chloroform, however, slow decomposition occurred at ambient temperature. Methylation of **2a** and **2b** was effected by methyl trifluoromethanesulfonate (methyl triflate) in diethyl ether at -50°C . Compounds **4a** and **4b** were isolated as orange, air- and moisture-sensitive powders, which are highly soluble in



2-5: R = *t*Bu (**a**), Ph (**b**)

Scheme 3. Reaction of **2a,b** with HBF_4 , $\text{CH}_3\text{OSO}_2\text{CF}_3$ and $\text{Me}_3\text{SiOSO}_2\text{CF}_3$

halogenated hydrocarbons. In the ^{31}P NMR spectrum, the protonated products **3a** and **3b** display doublets at $\delta = -53.7$ ($^1J_{\text{PH}} = 245$ Hz) and $\delta = -46.6$ ($^1J_{\text{PH}} = 257.7$ Hz) which are significantly shifted to high field with respect to the corresponding signals in **2a** ($\delta = 26.4$) and **2b** ($\delta = 31.3$). The size of the $^{31}\text{P}\{^1\text{H}\}$ coupling constants furthers the idea that the protonation occurred at the phosphorus center of the phosphoalkene. The resonances of the ^{13}C nuclei of the PCN_2 and the PC=O groups of the starting materials **2a** [$\delta = 201.4$ (d, $^1J_{\text{PC}} = 80.5$ Hz), 231.4 (d, $^1J_{\text{PC}} = 90.8$ Hz)] and **2b** [$\delta = 199.3$ (d, $^1J_{\text{PC}} = 78.5$ Hz), 215.6 (d, $^1J_{\text{PC}} = 78.7$ Hz)] are also high-field shifted upon protonation, and are observed in **3a** as broad singlets at $\delta = 178.1$ and $\delta = 220.0$ and in **3b** at $\delta = 177.9$ and 204.8 , respectively. In the ^1H NMR spectrum a doublet at $\delta = 6.02$ ($^1J_{\text{PH}} = 245$ Hz) (**3a**) and at $\delta = 6.23$ ($^1J_{\text{PH}} = 257.7$ Hz) (**3b**) accounts for the PH unit.

The IR spectrum of **2a** shows a very strong $\nu(\text{CO})$ absorption at $\tilde{\nu} = 1563$ cm^{-1} , which is hypsochromically shifted in the carbenium ion of **3a** [$\nu(\text{CO}) = 1680$, 1597 cm^{-1}]. Similar observations were made with **2b** and **3b**. The methylation of **2a** and **2b** to yield the phosphanyl carbenium salts **4a** and **4b**, gave rise to high-field shifts of only 30–33 ppm in the ^{31}P NMR spectra. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra the ^{13}C nuclei of the methyl groups of **4a** and **4b** were observed as doublets at $\delta = 6.0$ ($^1J_{\text{PC}} = 13.3$ Hz) and $\delta = 5.0$ ($^1J_{\text{PC}} = 11.7$ Hz), respectively, which is consistent with an alkylation at the P-atom of the P-acyl phosphoalkenes. Upon methylation, the ^{13}C nuclei of the CN_2 and the PCO units of precursors **2a** and **2b** are shielded by 21.8–23.8 and 5.6–8.7 ppm, and the $^1J_{\text{PC}}$ coupling constants decreased from 80.5 and 90.8 Hz in **2a** to 44.0 and

60.6 Hz in **4a** and from 78.5 and 78.7 Hz in **2b** to 39.4 and 37.7 Hz in **4b**. Again the $\nu(\text{CO})$ bands in the IR spectra of the salts **4a** ($\tilde{\nu} = 1644$, 1588 cm^{-1}) and **4b** ($\tilde{\nu} = 1647$, 1587 cm^{-1}) are observed at higher wavenumbers than in the neutral phosphoalkenes **2a** and **2b**.

These observations compare well with carbonyl-stabilized ylides $\text{RC}(\text{O})\text{CH}=\text{PPh}_3$, their corresponding phosphonium salts $[\text{RC}(\text{O})\text{CH}_2\text{PPh}_3]^+\text{X}^-$, and their transition metal complexes, where the position of the $\nu(\text{CO})$ band in the IR spectra serves as a sensitive probe for their electronic situation. Thus, the IR spectra of the ylides $\text{MeC}(\text{O})\text{CH}=\text{PPh}_3$ and $\text{PhC}(\text{O})\text{CH}=\text{PPh}_3$ display strong carbonyl bands at $\tilde{\nu} = 1540$ and 1500 cm^{-1} , which upon protonation to the corresponding phosphonium ions were shifted to 1710 and 1665 cm^{-1} , respectively.^[12]

The silylation of **2a** and **2b** with equimolar amounts of trimethylsilyl triflate in diethyl ether gave the extremely air- and moisture-sensitive salts **5a** and **5b**, which were isolated as pale yellow oils (Scheme 3). Here, in contrast to the protonation and methylation of **2a** and **2b**, a deshielding of the ^{31}P NMR resonances to $\delta = 109.2$ (**5a**) and $\delta = 101.0$ (**5b**) was observed.

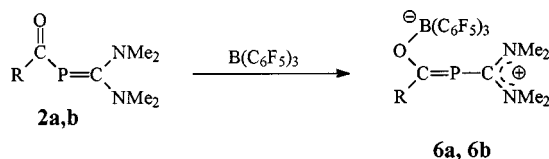
In the region typical for the stretching vibrations of acyclic carbonyl groups in the IR spectra of **5a** and **5b** no intense bands are present. This situation is best explained by an attack of the hard acid “ Me_3Si ” at the hard oxygen center of the carbonyl group with the formation of a Si–O and a P=C bond. Thus, the products can be regarded as salts with unsymmetrical phosphoallyl cations or, alternatively, as phosphoalkenyl-functionalized carbocations. Symmetrical phosphoallyl cations such as $[(\text{Me}_2\text{N})_2\text{CPC}(\text{NMe}_2)_2]^+^{[13]}$ or $[(t\text{BuC}^c-(t\text{Bu})\text{C}^b-\text{C}^a)_2\text{P}]^+(\text{C}^a-\text{C}^c)^{[2b]}$ were described several years ago. In the low-field region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **5a** and **5b**, doublets at $\delta = 180.8$ ($^1J_{\text{PC}} = 75.5$ Hz) and $\delta = 181.0$ ($^1J_{\text{PC}} = 72.4$ Hz) were attributed to the diaminocarbenium center, whereas the ^{13}C nuclei of the PCOSi units were observed as doublets at $\delta = 226.1$ ($^1J_{\text{PC}} = 77.3$ Hz) (**5a**) and $\delta = 211.8$ ($^1J_{\text{PC}} = 61.4$ Hz) (**5b**), respectively.

Thus, the main spectroscopic evidence for an electrophilic attack at the P- or O-atom of P-acyl phosphoalkenes with inverse electron density is taken from the direction in which the ^{31}P NMR resonance of the product is shifted. With this in mind, we decided to react **2a** and **2b** with the hard Lewis acids $\text{B}(\text{C}_6\text{F}_5)_3$, $t\text{Bu}_2\text{AlCl}$, and $(\text{AlMe}_3)_2$.

Treatment of **2a** or **2b** with tris(pentafluorophenyl)borane in toluene solution at room temperature gave the adducts **6a** or **6b** as yellow solids (Scheme 4).

The air- and moisture-sensitive compounds are only slightly soluble in dichloromethane or chloroform, but dissolve well in acetonitrile. In ethereal and hydrocarbon solvents **6a** and **6b** are insoluble. Low-field shifted singlets in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at $\delta = 68.3$ (**6a**) ($\Delta\delta = 41.9$) and 72.6 (**6b**) ($\Delta\delta = 41.5$), and the absence of $\nu(\text{C=O})$ bands in the IR spectra of the adducts agree with the ligation of the phosphoalkenes to the electron-deficient boron center via the oxygen atom. Doublets in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra at $\delta = 188.4$ ($^1J_{\text{PC}} = 89.0$ Hz) and 190.9 ($^1J_{\text{PC}} = 80.6$ Hz) are

readily assigned to the three-coordinate ^{13}C nuclei of the diaminocarbenium units in **6a** and **6b**. Low-field resonances at $\delta = 228.8$ (d, $^1J_{\text{PC}} = 81.4$ Hz, **6a**) and $\delta = 223.4$ ($^1J_{\text{PC}} =$



R = *t*Bu (**a**), Ph (**b**)

Scheme 4. Reaction of **2a,b** with $\text{B}(\text{C}_6\text{F}_5)_3$

71.1 Hz, **6b**) are due to the ^{13}C nuclei of the PCOB units.

X-ray Structural Analysis of **6b**

To confirm the spectroscopic evidence for the ligation of the phosphorane to the borane, an X-ray structural analysis of **6b** was performed (Figure 1, Table 1). Single crystals of **6b** were grown from toluene at -30°C . The analysis confirms the presence of a tetracoordinate boron atom, which is attached to the carbonyl group via a single bond of 1.506(3) Å. Delocalization of the negative charge into the C=O bond is obvious from an elongation from 1.240(2) Å (as measured in **2b**)^[14] to 1.315(3) Å and by the bond length P(1)–C(1) of 1.735(2) Å, which is similar to the P=C bond length in $\text{HP}=\text{C}(\text{NMe}_2)_2$ [1.740(1) Å].^[5] The trigonal-planar carbon atom C(1) (sum of angles 359.9°) is linked

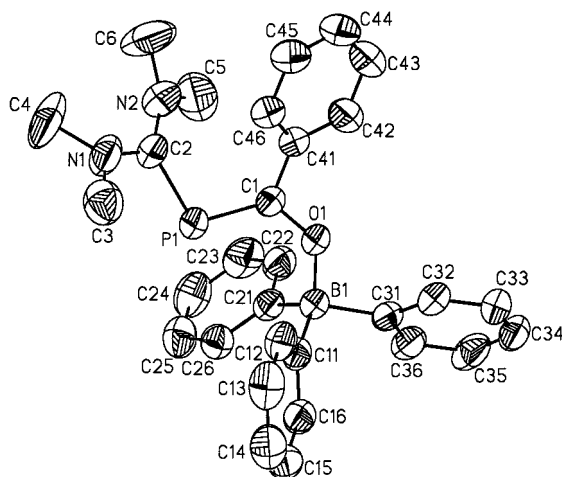
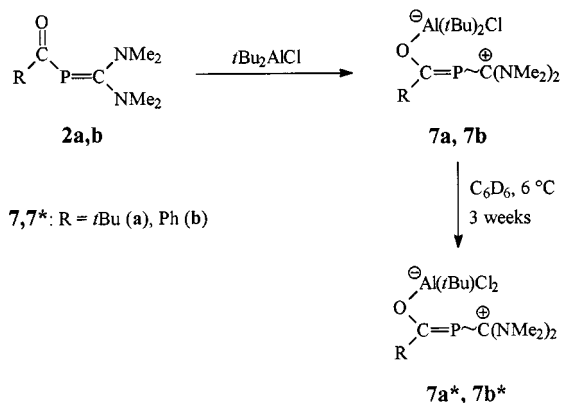


Figure 1. Molecular structure of **6b** in the crystal (fluorine atoms at the borane unit are omitted for clarity); selected bond lengths [Å] and angles $^\circ$: P(1)–C(1) 1.735(2), P(1)–C(2) 1.838(3), O(1)–C(1) 1.315(3), O(1)–B(1) 1.506(3), B(1)–C(11,21,31) av. 1.649(4), C(1)–C(41) 1.482(3), N(1)–C(2) 1.333(4), N(2)–C(2) 1.327(4), N(1)–C(3) 1.459(4), N(1)–C(4) 1.481(4), N(2)–C(5) 1.465(5), N(2)–C(6) 1.474(5), C(1)–P(1)–C(2) 102.3(1), C(1)–O(1)–B(1) 130.2(2), O(1)–C(1)–C(41) 111.0(2), P(1)–C(1)–O(1) 121.4(2), P(1)–C(1)–C(41) 127.5(2), P(1)–C(2)–N(1) 115.6(2), P(1)–C(2)–N(2) 123.6(2), N(1)–C(2)–N(2) 120.2(3), C(2)–N(1)–C(3) 122.7(2), C(2)–N(1)–C(4) 122.8(3), C(3)–N(1)–C(4) 113.8(3), C(2)–N(2)–C(5) 122.7(3), C(2)–N(2)–C(6) 122.3(4), C(5)–N(2)–C(6) 114.0(4), O(1)–B(1)–C(11) 111.1(2), O(1)–B(1)–C(21) 115.4(2), O(1)–B(1)–C(31) 107.0(3), C(11)–B(1)–C(21) 115.4(2), C(11)–B(1)–C(31) 107.0(2), C(21)–B(1)–C(31) 112.1(2).

to atom C(41) by a single bond of 1.482(3) Å. The former PC(N) bond in **2b** [1.800(1) Å] is lengthened to 1.838(3) Å in **6b**. The trigonal-planar carbon atom C(2) (sum of angles 359.4°) shows multiple bonding to the planarly configured nitrogen atoms [N(1)–C(2) = 1.333(4); N(2)–C(2) = 1.327(4) Å]. The bond angle C(1)–P(1)–C(2) [102.3(1) $^\circ$] is close to the value found in $\text{HP}=\text{C}(\text{NMe}_2)_2$ [103(1) $^\circ$].^[5] This is presumably because of the steric hinderance between the *cis*-oriented diaminocarbenium group and the phenyl ring which means that the valence angle P(1)–C(1)–C(41) [127.5(2) $^\circ$] is markedly more obtuse than P(1)–C(1)–O(1) [121.4(2) $^\circ$]. The very bulky $\text{B}(\text{C}_6\text{F}_5)_3$ moiety is directed towards the P-atom of the PC multiple bond, giving rise to torsion angles B(1)–O(1)–C(1)–P(1) and B(1)–O(1)–C(1)–C(41) of 2.5° and -179.4° , respectively. The torsion angle C(2)–P(1)–C(1)–O(1) was determined to be -175.1° . Thus, the atoms B(1), O(1), C(1), C(41), P(1) and C(2) are located in one plane, and the molecule may be described as a zwitterionic phosphorane, where the positive charge is formally centered at the diaminocarbenium substituent, and a negative charge at the boron atom.

Reaction of **2a** and **2b** With *t*Bu₂AlCl

Di-*tert*-butylaluminium chloride smoothly reacted with an equimolar amount of **2a** or **2b** in toluene at -30°C to afford the adducts **7a** or **7b** (Scheme 5). They were obtained as extremely moisture-sensitive orange solids. Attempts to grow crystals of **7a** and **7b** from C_6D_6 solution at 6°C within a period of 3 weeks led to the formation of crystalline $\text{RC}[\text{OAl}(\text{tBu})\text{Cl}_2]=\text{PC}(\text{NMe}_2)_2$ [R = *t*Bu (**7a***), Ph (**7b***)] instead.



Scheme 5. Reaction of **2a,b** with tBu_2AlCl

In the IR spectra of the adducts **7a** and **7b**, no unambiguous identification of $\nu(\text{CO})$ bands was possible. The ^1H NMR spectrum of **7a** was characterized by a singlet for the nine protons of the *tert*-butyl group at the P=C function, and by another singlet accounting for the 18 protons of the *tert*-butyl groups at the aluminium atom. A singlet at $\delta = 2.63$ was assigned to the protons of the dimethylamino groups.

In the low-field region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **7a** and **7b**, doublets at $\delta = 184.4$ ($^1J_{\text{PC}} = 76.5$ Hz) and

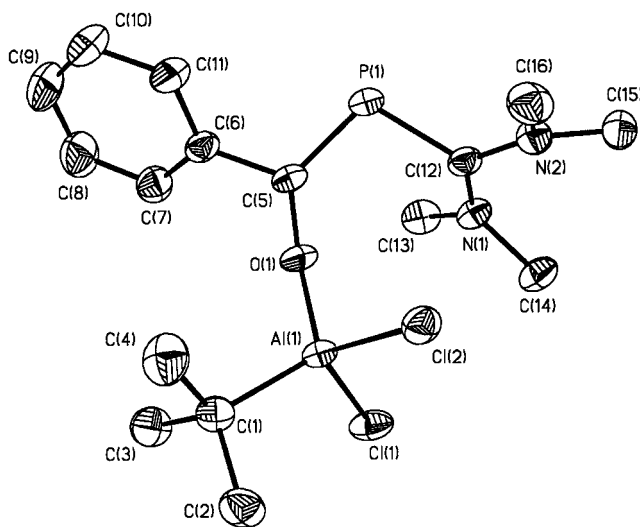
Table 1. Important bond lengths of compounds **2b**, **6b**, **7b***, **10a**, **11a**, and **12a** in Å

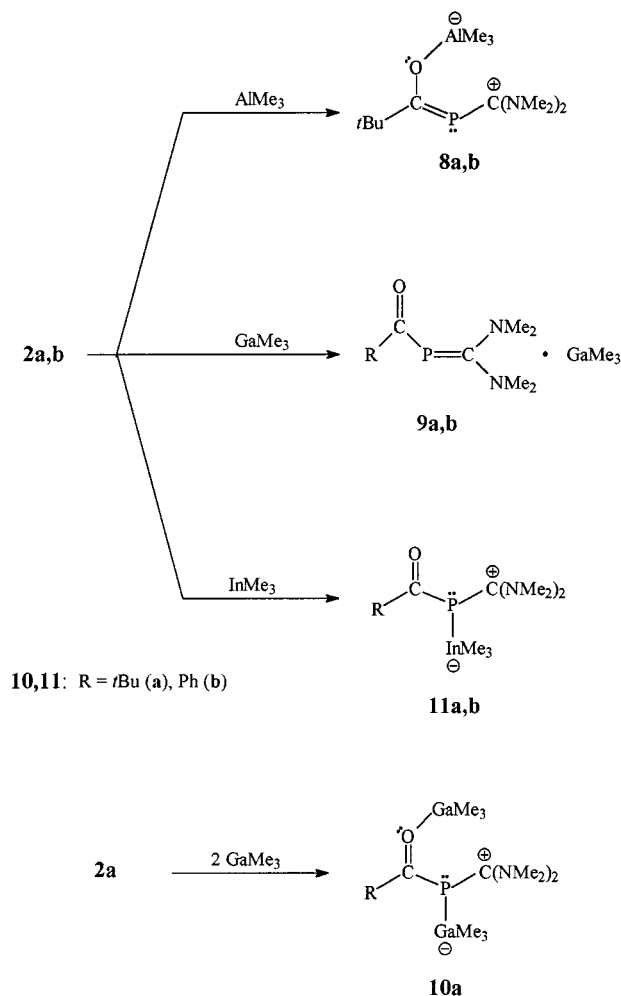
Comp.	M	d(C=O)	d[PC(O)]	d[PC(N)]	d(M–P)	d(M–O)
2b	—	1.240(2)	1.805(1)	1.800(1)	—	—
6b	B	1.315(3)	1.735(2)	1.838(3)	—	1.506(3)
7b*	Al	1.309(2)	1.728(2)	1.844(2)	—	1.776(1)
10a	Ga	1.249(3)	1.784(3)	1.831(3)	2.635(2)	2.109(2)
11a	In	1.238(10)	1.851(9)	1.823(8)	2.774(4)	—
12a	Cr	1.225(2)	1.848(2)	1.833(2)	2.516(1)	—

185.3 ($^1J_{\text{PC}} = 71.8$ Hz) were found for the carbon atoms of the diaminocarbenium unit. Again, adduct formation is accompanied by a high-field shift [$\Delta\delta = 17.0$ (**7a**) and 14.0 (**7b**)] for the signals of these nuclei. The carbon atoms adjacent to the oxygen atoms of **7a** and **7b** appeared as doublets at $\delta = 233.8$ ($^1J_{\text{PC}} = 86.5$ Hz) and 220.3 ($^1J_{\text{PC}} = 69.8$ Hz). Diagnostic for the mode of coordination are the $^{31}\text{P}\{^1\text{H}\}$ NMR resonances of both adducts which were observed at lower field (**7a**: $\delta = 72.9$ s; **7b**: 78.2 s) than in **2a** and **2b**. Thus, the presence of dative Al–O bonds in **7a** and **b** was inferred.

X-ray Structural Analysis of **7b***

Unfortunately, the initially obtained compounds **7a** and **b** were converted into **7a*** and **b*** during attempts to grow



Scheme 6. Reaction of **2a,b** with AlMe₃, GaMe₃ and InMe₃

minium atom is attached to the oxygen atom of the carbonyl group, as it was in the case of the adducts **7**. In the low-field region of the ¹³C{¹H} NMR spectrum doublets at $\delta = 184.4$ ($^1J_{\text{PC}} = 76.6$ Hz) and $\delta = 233.8$ ($^1J_{\text{PC}} = 86.5$ Hz) are readily assigned to the ¹³C nuclei of the CN₂ and OCP moieties, respectively. Signals due to the methyl groups at the metal atom were observed at $\delta = -5.2$ in the ¹³C NMR spectrum and $\delta = -0.37$ in the ¹H NMR spectrum. Similar results are obtained with **2b** and AlMe₃.

Under analogous conditions, one equivalent of trimethylgallium was added to **2a** and **2b**. The products were a very thermolabile yellow oil (**9a**) and a yellow powder (**9b**). Both compounds can easily be freed from Me₃Ga in vacuum at room temperature. Broad singlets in the ³¹P{¹H} NMR spectra at $\delta = 38.7$ (**9a**) or $\delta = 48.1$ (**9b**) did not allow for unambiguous assignment of the structure to one of the modes of coordination under discussion. In the presence of excess trimethylgallium, the NMR resonances did not shift significantly. However, when the mixture of **2a** and 2 equivalents of Me₃Ga in *n*-pentane was carefully concentrated to ca 2 mL, and this solution stored for 24 h at -30°C , yellow crystals of the 1:2 adduct **10a** were isolated. The NMR spectra of **10a** in C₆D₆ did not differ significantly from

those already registered for **9a**. As observed for **9a**, adduct **10a** easily lost the two molecules of Me₃Ga in a vacuum.

The coordination chemistry of **2a** and **b** towards the "soft" Lewis base InMe₃ is more straightforward (Scheme 6). The yellow solid adduct **11a** and the yellow oily adduct **11b** were obtained under similar conditions, and display singlets in their ³¹P{¹H} NMR spectra at $\delta = 15.6$ and 36.8 . A high-field coordination shift of $\Delta\delta = 10.8$ for **11a**, and a low-field shift of $\Delta\delta = 5.5$ is consistent with an In–P contact rather than with the alternative In–O ligation. In the low-field part of the ¹³C{¹H} NMR spectrum, doublets at $\delta = 195.5$ ($^1J_{\text{PC}} = 68.4$ Hz) and 234.0 ($^1J_{\text{PC}} = 84.5$ Hz) (**11a**) and $\delta = 196.2$ ($^1J_{\text{PC}} = 76.6$ Hz) and 219.9 ($^1J_{\text{PC}} = 76.7$ Hz) (**11b**) are caused by the ¹³C atoms of the diaminocarbenium- and the carbonyl-groups, respectively. In the IR spectrum of **11a**, strong $\nu(\text{CO})$ bands appears at $\tilde{\nu} = 1594$ and 1546 cm^{-1} , and in the spectrum of **11b**, a medium intense $\nu(\text{CO})$ band at 1540 cm^{-1} with a shoulder at 1597 cm^{-1} was observed.

X-ray Structural Analysis of **10a**

The crystal structure analysis of **10a** shed some light on the nature of the 1:2 adduct (Figure 3, Table 1). The backbone of the molecule constitutes a P-acyl unit with a trigonal-pyramidal P-atom (sum of angles 333.26°), which is connected to the atoms C(4), C(12) and Ga(2) by single bonds. The bond length P(1)–C(4) [$1.784(3)\text{ \AA}$] is shorter than P(1)–C(12) [$1.831(3)\text{ \AA}$], which was determined to be $1.800(1)\text{ \AA}$ in **2b**. A pronounced bond strengthening of the P–C_(CO) bond as encountered in **6b** and **7b*** did not occur. The atomic distance Ga(2)–P of $2.635(2)\text{ \AA}$ is markedly longer than in the complex $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{-FeP}\{\text{GaMe}_3\}\text{C}(\text{NMe}_2)_2]$ [$2.503(2)\text{ \AA}$].^[16] Generally, Ga–P bonds in molecules with tetracoordinate gallium and phosphorus range from $2.347(5)\text{ \AA}$ in $[(\text{Me}_3\text{Si})_3\text{P}\rightarrow\text{GaI}_3]$ ^[17] up to $2.683(5)\text{ \AA}$ in $[\text{Ph}_2(\text{H})\text{P}\rightarrow\text{Ga}\{\text{CH}_2(\text{tBu})\}_3]$.^{[18][19]} The second molecule of GaMe₃ is bound to the oxygen atom of the carbonyl group by a long dative bond [Ga(1)–O(1) = $2.109(2)\text{ \AA}$]. As the covalent radii of Al ($1.25\text{ \AA}$) and Ga ($1.26\text{ \AA}$)^[20] are similar, it is obvious from the comparison with the Al–O contact in **7b*** that only a weak gallium–oxygen bond is present in **10a**.

The bond length of the carbonyl group [$1.249(3)\text{ \AA}$] is similar to that of the P-acyl function in **2b** [$1.240(2)\text{ \AA}$]. The weak contact between the oxygen atom and the gallane may also be inferred from the small deviation of the Ga(CH₃)₃ unit from planarity [sum of angles C(1)–Ga(1)–C(2), C(1)–Ga(1)–C(3), C(2)–Ga(1)–C(3) = 350.3°]. For comparison, a more pronounced perturbation of the planar configuration of the borane by adduct formation with **2b** is evident by the corresponding sum of angles C(11)–B(1)–C(21), C(11)–B(1)–C(31) and C(21)–B(1)–C(31) of 334.5° in **6b**. In the aluminium adduct **7b***, the respective sum of angles (332.94°) is similar to **6b**. Moreover, the angle at the carbonyl oxygen atom opens up in going from **6b** [$130.2(2)^\circ$] through **7b*** [$139.2(1)^\circ$] to **10a** [$148.7(2)^\circ$].

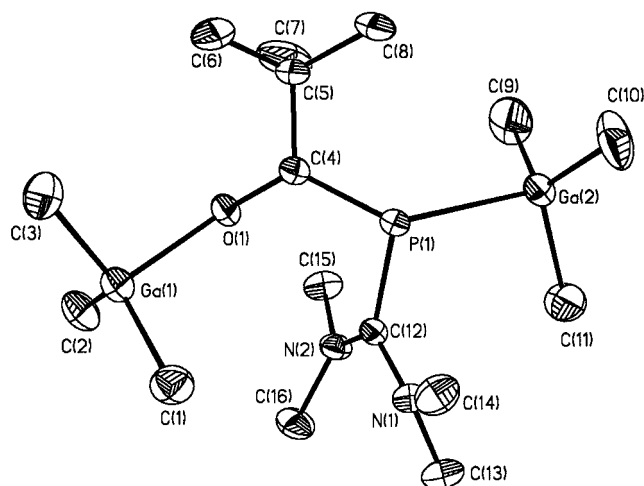


Figure 3. Molecular structure of **10a** in the crystal; selected bond lengths [Å] and angles [°]: P(1)–C(4) 1.784(3), P(1)–C(12) 1.831(3), P(1)–Ga(2) 2.635(2), O(1)–C(4) 1.249(3), O(1)–Ga(1) 2.109(2), C(4)–C(5) 1.537(3), Ga(1)–C(1) 1.985(3), Ga(1)–C(2) 1.972(3), Ga(1)–C(3) 1.962(3), Ga(2)–C(9) 1.976(3), Ga(2)–C(10) 1.965(3), Ga(2)–C(11) 1.980(3), N(1)–C(12) 1.337(3), N(2)–C(12) 1.337(3), N(1)–C(13) 1.465(3), N(1)–C(14) 1.470(3), N(2)–C(15) 1.462(3), N(2)–C(16) 1.470(3); C(4)–P(1)–C(12) 102.9(1), C(4)–P(1)–Ga(2) 127.7(1), Ga(2)–P(1)–C(12) 102.6(1), P(1)–C(4)–O(1) 124.2(2), P(1)–C(4)–C(5) 118.4(2), O(1)–C(4)–C(5) 117.5(2), Ga(1)–O(1)–C(4) 148.7(2), P(1)–C(12)–N(1) 116.7(2), P(1)–C(12)–N(2) 123.5(2), N(1)–C(12)–N(2) 119.4(2), C(12)–N(1)–C(13) 123.3(2), C(12)–N(1)–C(14) 122.3(2), C(13)–N(1)–C(14) 113.5(2), C(12)–N(2)–C(15) 123.0(2), C(12)–N(2)–C(16) 123.2(2), C(15)–N(2)–C(16) 113.2(2), O(1)–Ga(1)–C(1) 103.5(1), O(1)–Ga(1)–C(2) 97.0(1), O(1)–Ga(1)–C(3) 101.1(1), C(1)–Ga(1)–C(2) 117.6(1), C(2)–Ga(1)–C(3) 117.5(1), C(1)–Ga(1)–C(3) 115.2(1), P(1)–Ga(2)–C(9) 107.6(1), P(1)–Ga(2)–C(10) 99.8(1), P(1)–Ga(2)–C(11) 98.8(1), C(9)–Ga(2)–C(10) 118.8(2), C(9)–Ga(2)–C(11) 112.8(2), C(10)–Ga(2)–C(11) 115.5(2)

X-ray Structural Analysis of **11a**

The X-ray structural analysis of **11a** has fully confirmed the conclusions drawn from the spectra (Figure 4, Table 1). A trigonal pyramid configured phosphorus atom is coordinated to the indium atom by a single bond of 2.774(4) Å. This value is similar to those measured in (Me₃In)₂(Ph₂PCH₂CH₂PPh₂) [2.755(4) Å].^[21] For indane-phosphane adducts In–P bond lengths in the range of 2.575(3) to 2.819(2) Å have been reported.^[19a] The coordination of **2a** to the planar acceptor molecule InMe₃ causes only a small pyramidalization of the InC₃-unit, as may be concluded from the sum of the angles C(1)–In(1)–C(2), C(1)–In(1)–C(3) and C(2)–In(1)–C(3) (349.8°). The environment of carbon atom C(4) is trigonal-planar, a C=O double bond of 1.238(10) Å and a C–C single bond of 1.552(11) Å to the *tert*-butyl substituent clearly exclude π -conjugation of the carbonyl group with the lone pair on phosphorus in **11a**. Whereas similar C=O bond lengths were encountered in acyl phosphanes such as [(η^5 -C₅Me₅)(CO)₂Ru–C(O)P(*t*Bu)(SiMe₃)] [1.219(4) Å]^[22] or *t*BuC(O)P(Ph)P(Ph)C(O)*t*Bu (1.21 Å),^[23] the P–C(CO) single bonds in these molecules are considerably longer [1.952(3) Å and 1.89 Å, respectively] than in **11a** [P(1)–C(4) = 1.851(9) Å]. The structural features of the diaminocarbon-

ium unit are similar to those in **6b**, **7b*** and **10a**. Again this group is linked to the P-atom through a single bond [P(1)–C(9) = 1.823(8) Å].

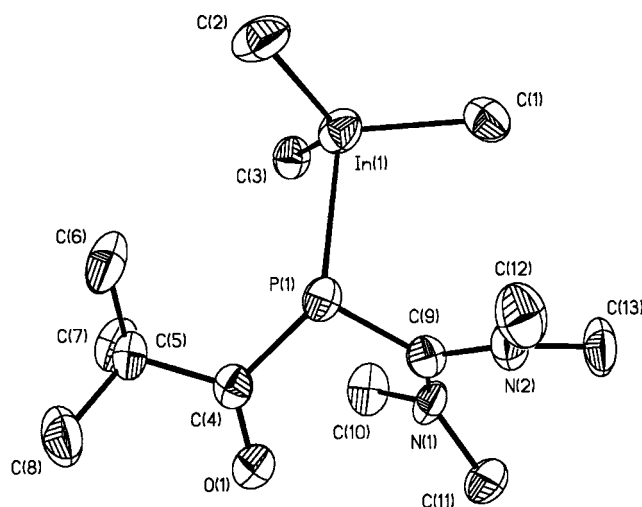


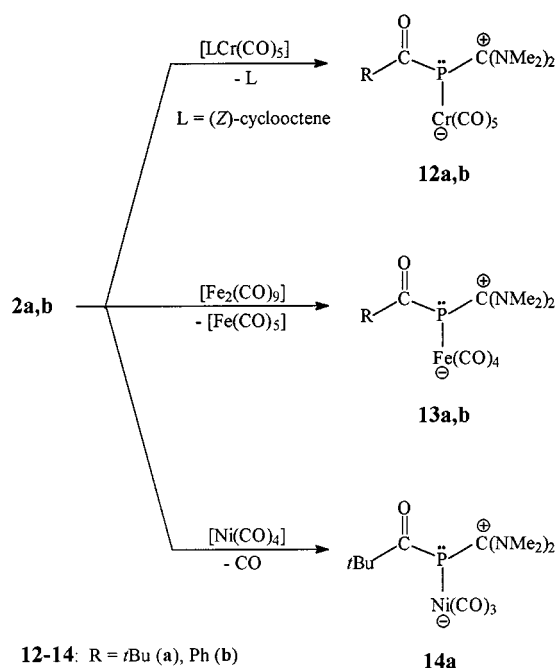
Figure 4. Molecular structure of **11a** in the crystal; selected bond lengths [Å] and angles [°]: P(1)–C(4) 1.851(9), P(1)–C(9) 1.823(8), P(1)–In(1) 2.774(4), O(1)–C(4) 1.238(10), C(4)–C(5) 1.552(11), N(1)–C(9) 1.334(10), N(2)–C(9) 1.374(10), N(1)–C(10) 1.483(10), N(1)–C(11) 1.483(10), N(2)–C(12) 1.452(12), N(2)–C(13) 1.497(12), In(1)–C(1) 2.198(9), In(1)–C(2) 2.189(9), In(1)–C(3) 2.216(8); C(4)–P(1)–C(9) 101.2(4), C(4)–P(1)–In(1) 125.9(3), In(1)–P(1)–C(9) 102.3(3), P(1)–C(4)–O(1) 122.2(6), O(1)–C(4)–C(5) 119.8(7), P(1)–C(4)–C(5) 118.0(6), P(1)–C(9)–N(1) 125.5(6), P(1)–C(9)–N(2) 117.3(6), N(1)–C(9)–N(2) 117.1(7), C(9)–N(1)–C(10) 122.7(7), C(9)–N(1)–C(11) 123.6(7), C(10)–N(1)–C(11) 112.7(7), C(9)–N(2)–C(12) 124.4(8), C(9)–N(2)–C(13) 122.0(8), C(12)–N(2)–C(13) 113.1(8), P(1)–In(1)–C(1) 97.6(3), P(1)–In(1)–C(2) 98.9(3), P(1)–In(1)–C(3) 105.5(2), C(1)–In(1)–C(2) 115.8(4), C(2)–In(1)–C(3) 119.9(4), C(1)–In(1)–C(3) 114.1(3)

Reaction of **2a** and **2b** With [(*Z*-cyclooctene)Cr(CO)₅], [Fe₂(CO)₉] and [Ni(CO)₄]

With regard to the concept of hard and soft acids and bases, and under consideration the coordination chemistry of carbonyl-stabilized ylides, the reaction of β -acyl phosphoalkenes with low valent transition metal carbonyls should lead to complexes with metal-phosphorus bonding. To further substantiate this idea the phosphoalkenes **2a** and **b** were reacted with equimolar amounts of [(*Z*-cyclooctene)Cr(CO)₅] for 2 h in diethyl ether (**2a**) or *n*-pentane (**2b**). The pentacarbonylchromium complexes **12a** and **12b** were isolated as yellow or orange-red microcrystalline solids in 79% and 71% yield, respectively.

The red microcrystalline tetracarbonyliron complexes **13a** and **13b** (73–76% yield) resulted from the treatment of **2a** and **b** with equimolar amounts of solid [Fe₂(CO)₉] in diethyl ether at room temperature for 18–20 h.

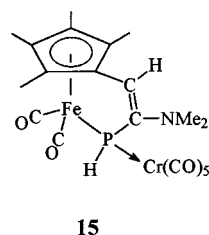
Compound **2a** and [Ni(CO)₄] underwent reaction in diethyl ether to afford complex **14a** as an orange crystalline,

Scheme 7. Complexation of **2a,b** with transition metal carbonyls

extremely light-sensitive solid. Purification of this product was effected by recrystallization from diethyl ether at -30°C . Attempts to synthesize the analogous nickeltricarboxyl complex of **2b** failed (Scheme 7).

High-field shifts of the $^{31}\text{P}\{^1\text{H}\}$ NMR resonances of complexes **12a**, **12b**, **13a**, **13b**, and **14a** in the range of $\delta = -26.4$ to 1.9 are consistent with metal–phosphorus ligation. In the low-field region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **12a**, **13a** and **14a** the ^{13}C atoms of the pivaloyl substituents were observed as doublets at $\delta = 232.2$ to 235.3 ($^1J_{\text{PC}} = 70.6$ to 80.0 Hz). Doublets at $\delta = 195.2$ to 198.7 ($^1J_{\text{PC}} = 48.0$ to 55.4 Hz) are readily assigned to the tri-coordinate carbon atoms of the carbenium building block. Similar observations have been made in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of P-benzoyl analogues.

Information on the σ -donor/ π -acceptor properties of **2a** and **b** were provided by the IR spectra of the carbonylmetal complexes. Three intense bands at $\tilde{\nu} = 2054$, 1976 and 1966 cm^{-1} in the IR spectrum of **14a** (KBr) are attributed to the stretching modes of the CO ligands of the $[\text{Ni}(\text{CO})_3]$ moiety. The local symmetry of the latter is lower than that of the point group C_{3v} . The donor capacity of the inversely polarized phosphalkene is similar to that of PtBu_3 in $[(t\text{Bu}_3\text{P})\text{Ni}(\text{CO})_3]$ [$\nu(\text{CO})$ (CH_2Cl_2) = 2056 , 1971 cm^{-1}].^[24] It is interesting to note that the metallocphosphalkene $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeP}=\text{C}(\text{NMe}_2)_2]$ of inverse electron density behaves as a much stronger donor ligand towards the $[\text{Ni}(\text{CO})_3]$ group in $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeP}\{\text{Ni}(\text{CO})_3\}\text{-C}(\text{NMe}_2)_2]$ [$\nu(\text{NiCO})$ (KBr) = 2034 , 1957 , 1917 cm^{-1}].^[7b] The observation of three intense carbonyl bands in the IR spectrum of the tetracarbonyliron complex **13a** ranging from 2028 to 1927 cm^{-1} is consistent with the local symmetry of the point group C_{3v} for the $[\text{Fe}(\text{CO})_4]$ -unit with an



additional donor ligand in the axial position at the trigonal bipyramid. Intense carbonyl absorptions at $\tilde{\nu} = 2051$, 1987 , 1919 and 1900 cm^{-1} in the IR spectrum of **12a** (KBr) correspond to the $\nu(\text{CO})$ bands in phosphane complex **15** ($\tilde{\nu} = 2051$, 1989 , 1927 , 1894 cm^{-1}).^[7b] Similar absorptions occur in compounds **12b** and **13b**.

In the IR spectra of complexes **12a**, **13a**, and **14a**, medium to intense bands at $\tilde{\nu} = 1584$ to 1596 and 1542 to 1560 cm^{-1} are tentatively assigned to the $\nu(\text{CO})$ modes of the pivaloyl substituent. Thus they are found between those of free **2a** and its protonation and methylation products **3a** and **4a**. For comparison, coordination of the ylides $\text{MeC}(\text{O})\text{CH}=\text{PPh}_3$ and $\text{PhC}(\text{O})\text{CH}=\text{PPh}_3$ to AuCl via the C-atom has also led to hypsochromic shifts of the $\nu(\text{CO})$ bands from 1540 to 1645 and from 1500 to 1620 cm^{-1} .^[12]

X-ray Structural Analysis of **12a**

An ORTEP drawing of **12a** is shown in Figure 5; selected bond lengths and angles are given in the caption and in Table 1. The molecule exhibits octahedral geometry at the metal atom; one coordination site is occupied by an η^1 -ligated phosphalkene. The complexation of $t\text{BuC}(\text{O})\text{P}=\text{C}(\text{NMe}_2)_2$ to the $[\text{Cr}(\text{CO})_5]$ moiety is accompanied by a severe distortion of the organophosphorus ligand. A single bond of $1.833(2)$ Å is found between the trigonal pyramidal phosphorus atom (sum of angles 332.9°) and the planar carbon atom C(6) (sum of angles 359.9°). Both nitrogen atoms are also planar (sum of angles 359.9 and 358.5°). The bond length $\text{P}(1)\text{--C}(1)$ [$1.848(2)$ Å] is as long as the other $\text{P}\text{--C}$ single bond in the molecule. The carbon atom C(1) is trigonal planar configured (sum of angles 359.4°) featuring a $\text{C}=\text{O}$ double bond of $1.225(2)$ Å and a $\text{C}\text{--C}$ single bond of $1.541(2)$ Å to the *tert*-butyl substituent, which clearly excludes any significant π -conjugation between the carbonyl group and the lone pair on phosphorus in **12a**. The $\text{Cr}\text{--P}$ bond length [$2.516(1)$ Å] is similar to that in $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeP}\{\text{Cr}(\text{CO})_5\}\text{C}(\text{NMe}_2)_2]$ [$2.533(2)$ Å],^[7a] but clearly exceeds the $\text{Cr}\text{--P}$ atomic distances in complexes such as $[2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{P}\{\text{Cr}(\text{CO})_5\}=\text{CPh}_2]$ [$2.356(1)$ Å]^[6a] or $[\text{CF}_3\text{P}\{\text{Cr}(\text{CO})_5\}=\text{C}(\text{F})\text{NMe}_2]$ [$2.454(1)$ Å].^[3a] A view perpendicular to the $[\text{Cr}(\text{CO})_4]$ plane indicates an almost eclipsed conformation with torsion angles $\text{C}(1)\text{--P}(1)\text{--Cr}(1)\text{--C}(14) = 11.3^\circ$ and $\text{C}(6)\text{--P}(1)\text{--Cr}(1)\text{--C}(13) = -11.2^\circ$ (Figure 6).

Presumably due to steric hindrance, the ideal local C_{4v} -symmetry of the $[\text{Cr}(\text{CO})_5]$ unit is slightly perturbed, as it is evident from the angles $\text{C}(11)\text{--Cr}(1)\text{--C}(15)$ [$86.8(1)^\circ$],

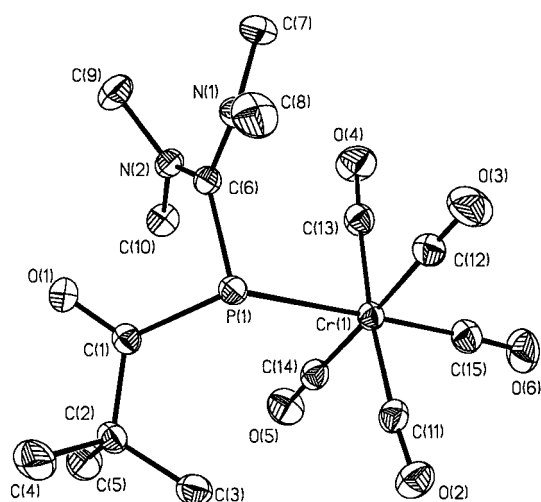


Figure 5. Molecular structure of **12a** in the crystal; selected bond lengths [Å] and angles [°]: Cr(1)–P(1) 2.516(1), Cr(1)–C(11) 1.897(2), Cr(1)–C(12) 1.889(2), Cr(1)–C(13) 1.899(2), Cr(1)–C(14) 1.924(2), Cr(1)–C(15) 1.853(2), P(1)–C(1) 1.848(2), C(1)–O(1) 1.225(2), C(1)–C(2) 1.541(2), P(1)–C(6) 1.833(2), C(6)–N(1) 1.347(2), C(6)–N(2) 1.339(2), N(1)–C(7) 1.471(2), N(1)–C(8) 1.466(3), N(2)–C(9) 1.469(2), N(2)–C(10) 1.465(2), C(2)–C(1)–P(1) 120.5(1), C(2)–C(1)–O(1) 118.0(2), P(1)–C(1)–O(1) 120.9(1), C(1)–P(1)–Cr(1) 130.0(1), C(1)–P(1)–C(6) 98.5(1), Cr(1)–P(1)–C(6) 104.4(1), P(1)–C(6)–N(1) 117.7(1), P(1)–C(6)–N(2) 124.3(1), N(1)–C(6)–N(2) 118.0(2), C(6)–N(1)–C(7) 123.1(2), C(6)–N(1)–C(8) 123.5(2), C(7)–N(1)–C(8) 113.3(2), C(6)–N(2)–C(9) 122.5(2), C(6)–N(2)–C(10) 123.4(1), C(9)–N(2)–C(10) 112.6(2), P(1)–Cr(1)–C(11) 90.9(1), P(1)–Cr(1)–C(12) 87.6(1), P(1)–Cr(1)–C(13) 92.1(1), P(1)–Cr(1)–C(14) 91.1(1), P(1)–Cr(1)–C(15) 177.6(1), C–Cr–C 86.8(1)–92.4(1), Cr–C–O 175.0(2)–178.2(2).

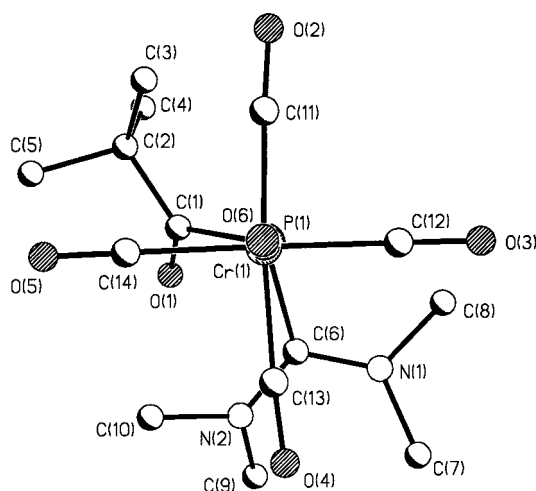


Figure 6. Newman projection of **12a** along the Cr(1)–P(1) vector

P(1)–Cr(1)–C(13) [92.1(1)°] and C(11)–Cr(1)–C(13) [174.6(1)°]. It is also remarkable that one of the equatorial Cr–C(CO) bonds [Cr(1)–C(14) = 1.924(2) Å] is elongated in comparison to the remaining equatorial carbonyl ligands [Cr–CO = 1.889(2) to 1.899(2) Å]. As usual in [Cr(CO)₅] complexes with donor ligands, the axial Cr–CO bond is markedly shortened [Cr(1)–C(15) = 1.853(2) Å]

Experimental Section

All reactions were performed by Schlenk techniques under an atmosphere of dry nitrogen. The phosphaaalkenes $\text{Me}_3\text{SiP}=\text{C}(\text{NMe}_2)_2$ **1**,^[25] **2a**,**b**,^[9] $t\text{Bu}_2\text{AlCl}$,^[26] and the complexes $[\text{Fe}_2(\text{CO})_9]$ ^[27] and $\{(\text{Z})\text{-cyclooctene}\}\text{Cr}(\text{CO})_5$ ^[28] were prepared as described in the literature. $[\text{Ni}(\text{CO})_4]$, $\text{HBF}_4\cdot\text{OEt}_2$, $\text{MeOSO}_2\text{CF}_3$, $\text{Me}_3\text{SiOSO}_2\text{CF}_3$, $(\text{AlMe}_3)_2$, GaMe_3 and InMe_3 were purchased commercially. – Infrared spectra were recorded with a Bruker FTIR IFS 66 spectrometer. – NMR Spectra: Bruker AC 100, AM Avance DRX 500. Standards: SiMe_4 (^1H , ^{13}C), external 85% H_3PO_4 (^{31}P).

[rBuC(O)P(H)C(NMe₂)₂]BF₄ (**3a**): A solution of pivaloyl chloride (0.18 g, 1.47 mmol) in diethyl ether (10 mL) was added dropwise to a chilled solution (−50 °C) of **1** (0.30 g, 1.47 mmol) in diethyl ether (30 mL). The reaction mixture was warmed to −20 °C and stirred for 30 min. After cooling to −50 °C a solution of 20 mL (1.47 mmol) of ethereal HBF₄ (54%) in diethyl ether (10 mL) was added dropwise. The solution was slowly warmed to room temp. and stirred for 1 h. A colorless precipitate was formed, filtered off and washed with diethyl ether (20 mL) to afford 0.33 g (74% yield) of **3a**. – IR (KBr): $\tilde{\nu}$ = 1680 s, 1597 [s, C(=O)] cm^{−1}. – ¹H NMR (CD₂Cl₂): δ = 1.18 [s, 9 H, C(CH₃)₃], 3.24 (s, 12 H, NCH₃), 6.02 (d, J_{PH} = 245 Hz, 1 H, PH). – ¹³C{¹H} NMR (CD₂Cl₂): δ = 28.5 [s, C(CH₃)₃], 44.6 (s, NCH₃), 49.9 [s, C(CH₃)₃], 178.1 (s, br, CN₂), 220.0 (s, br, C=O); – ³¹P NMR (CD₂Cl₂): δ = −53.7 (d, J_{PH} = 245 Hz); – C₁₀H₂₂BF₄N₂OP (304.07): calcd. C 39.50, H 7.29, N 9.21; found C 39.43, H 7.03, N 9.23.

[PhC(O)P(H)C(NMe₂)₂]BF₄ (**3b**): A solution of **2b** was prepared analogously from benzoyl chloride (0.26 g, 1.81 mmol) and **1** (0.37 g, 1.81 mmol) in diethyl ether (40 mL). At -50°C 0.29 g (1.81 mmol) of ethereal HBF₄ (54%) in 10 mL of the same solvent was added dropwise. It was warmed to room temp. and stirred for 1 h. The supernatant solvent was decanted from a light-yellow oil. The latter was kept under vacuum (10⁻¹ Torr, 1 h) to afford 0.56 g (95%) of **3b** as a light yellow viscous oil. - IR (CsI, film): $\tilde{\nu}$ = 1653 (s), 1599 [s, (C=O)] cm⁻¹. - ¹H NMR (CD₂Cl₂, 22°C): δ = 3.34 (s, 12 H, NCH₃), 6.36 (s, br, 1 H, PH), 7.55 (m, 2 H, *m*-PhH), 7.70 (m, 1 H, *p*-PhH), 7.80 (m, 2 H, *o*-PhH). - ¹H NMR (CD₂Cl₂, -70°C): δ = 3.36 (s, 12 H, NCH₃), 6.23 (d, *J*_{PH} = 257.7 Hz, 1 H, PH), 7.65 (m, 3 H, *m,p*-PhH), 7.80 (m, 2 H, *o*-PhH). - ¹³C{¹H} NMR (CD₂Cl₂): δ = 45.0 (s, NCH₃), 127.0 s, 129.6 s, 135.5 s, 138.1 (d, *J*_{PC} = 31.8 Hz, PhC), 177.9 (s, br, CN₂), 204.8 (s, br, C=O). - ³¹P NMR (CD₂Cl₂, -70°C): δ = -46.6 (d, *J*_{PH} = 257.1 Hz). - C₁₄H₃₀BF₄N₂OP (324.06): calcd. C 44.48, H 5.60, N 8.64; found C 44.38, H 5.69, N 8.40.

[**rRuC(O)P(CH₃)C(NMe₂)₂][SO₃CF₃] (**4a**): As described before, **2a** was generated from equimolar amounts of **1** (0.38 g, 1.86 mmol) and pivaloyl chloride (0.23 g, 1.86 mmol) in 40 mL of diethyl ether. At -50°C a solution of methyl triflate (0.31 g, 1.86 mmol) in diethyl ether (10 mL) was added dropwise to the mixture, thereafter it was warmed to room temp. and stirred for 1 h. The orange precipitate formed was filtered off and washed with diethyl ether (30 mL) to give 0.53 g (75% yield) of **5a** as a moisture-sensitive solid. - IR (KBr): $\tilde{\nu}$ = 1644 s, 1588 [s, (C=O)] cm⁻¹. - ¹H NMR (CD₂Cl₂): δ = 1.20 [s, 9 H, C(CH₃)₃], 1.69 (d, J_{PH} = 4.5 Hz, 3 H, PCH₃), 3.32 (s, 12 H, NCH₃). - ¹³C{¹H} NMR (CD₂Cl₂): δ = 6.0 (d, J_{PC} = 13.3 Hz, PCH₃), 26.4 [s, C(CH₃)₃], 45.2 (s, NCH₃), 49.8 [d, J_{PC} = 30.4 Hz, C(CH₃)₃], 121.2 (q, J_{CF} = 321.0 Hz, CF₃), 177.6 [d, J_{PC} = 44.0 Hz, CN₂], 222.7 (d, J_{PC} = 60.6 Hz, C=O). - ³¹P{¹H} NMR: δ = -3.8 s. - C₁₂H₂₄F₃N₂O₄PS (380.36): calcd. C 37.89, H 6.36, N 7.36; found C 36.62, H 5.82, N 7.34.**

[PhC(O)P(CH₃)C(NMe₂)₂][SO₃CF₃] (4b): A solution of **2b**, prepared from **1** (0.32 g, 1.57 mmol) and benzoyl chloride (0.22 g,

1.57 mmol) in 40 mL of diethyl ether was treated with methyl triflate (0.25 g, 1.57 mmol) in diethyl ether (10 mL) at -50°C and then allowed to warm to room temperature with stirring. A pale orange solid formed, which was filtered off and washed with diethyl ether (30 mL) to afford 0.56 g (89%) of **4b**. – IR (CsI): $\tilde{\nu} = 1647$ m, 1587 [m, (C=O)] cm^{-1} . – ^1H NMR (CD_2Cl_2): $\delta = 1.78$ (d, $J_{\text{PH}} = 3.7$ Hz, PCH_3), 3.16 (s, 12 H, NCH_3), 7.57 (m, 3 H, PhH), 7.74 (m, 2 H, PhH). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 5.0$ (d, $J_{\text{PC}} = 11.7$ Hz, PCH_3), 44.6 (s, NCH_3), 121.1 (q, $J_{\text{CF}} = 321.2$ Hz, CF_3), 127.2 (d, $J_{\text{PC}} = 6.9$ Hz, PhC), 129.7 s, 136.0 s, 138.1 (d, $J_{\text{PC}} = 35.9$ Hz, PhC), 177.5 (d, $J_{\text{PC}} = 39.4$ Hz, CN_2), 210.0 (d, $J_{\text{PC}} = 37.7$ Hz, C=O). – $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = -2.3$ s. – $\text{C}_{14}\text{H}_{20}\text{F}_3\text{N}_2\text{O}_4\text{PS}$ (400.35): calcd. C 42.00, H 5.04, N 7.00; found C 42.00, H 5.00, N 6.70.

[*t*BuC(OSiMe₃)=PC(NMe₂)₂][SO₃CF₃] (5a**):** A solution of **2a**, obtained from **1** (0.28 g, 1.37 mmol) and pivaloyl chloride (0.17 g, 1.37 mmol) in 40 mL of diethyl ether was treated at -50°C with a solution of trimethylsilyl triflate (0.30 g, 1.37 mmol) in diethyl ether (10 mL). Thereafter it was warmed to room temp. whereupon a pale yellow oil separated. The solvent was decanted, and the remaining oil was kept in vacuo (10^{-2} Torr) for 1 h to afford 0.53 g (88% yield) of **5a** as a viscous, very air- and moisture-sensitive liquid. – IR (CsI, film): $\tilde{\nu} = 1221$ [m, $\delta(\text{SiMe}_3)$], 836 [m, $\rho(\text{SiMe}_3)$] cm^{-1} . – ^1H NMR (CD_2Cl_2): $\delta = 0.33$ (s, 9 H, SiCH_3), 1.24 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 3.33 (s, 12 H, NCH_3). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 1.7$ (s, SiCH_3), 28.5 [s, $\text{C}(\text{CH}_3)_3$], 45.0 (s, NCH_3), 51.1 [s, br, $\text{C}(\text{CH}_3)_3$], 121.2 (q, $J_{\text{CF}} = 321.3$ Hz, CF_3), 180.8 (d, $J_{\text{PC}} = 75.5$ Hz, CN_2), 226.1 (d, $J_{\text{PC}} = 77.3$ Hz, PCO). – $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 109.2$ s. – $\text{C}_{14}\text{H}_{30}\text{F}_3\text{N}_2\text{O}_4\text{PSSi}$ (438.52): calcd. C 38.35, H 6.90, N 6.39; found C 36.91, H 6.36, N 6.44.

PhC(OSiMe₃)=PC(NMe₂)₂][SO₃CF₃] (5b**):** A solution of **2b**, prepared from **1** (0.25 g, 1.23 mmol) and benzoyl chloride (0.17 g, 1.23 mmol), in 40 mL of diethyl ether was treated with a solution of 0.27 g (1.23 mmol) of trimethylsilyl triflate in the same solvent (10 mL) at -50°C . It was warmed to room temp., whereupon a colorless oil separated. Decanting the solvent and liberating the oil from volatile compounds in vacuo (10^{-2} Torr) gave 0.48 g of **5b** as an extremely air- and moisture-sensitive colorless oil. – IR (CsI, film): $\tilde{\nu} = 1223$ [m, $\delta(\text{SiMe}_3)$], 839 [m, $\rho(\text{SiMe}_3)$] cm^{-1} . – ^1H NMR (CD_2Cl_2): $\delta = 0.15$ (s, 9 H, SiCH_3), 3.39 (s, 12 H, NCH_3), 7.42 (m, 3 H, PhH), 7.59 (m, 2 H, PhH). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 0.8$ (s, SiCH_3), 45.1 (s, NCH_3), 127.1 s, 129.5 s, 139.5 (s, PhC), 181.0 (d, $J_{\text{PC}} = 72.4$ Hz, CN_2), 211.3 (d, $J_{\text{PC}} = 61.4$ Hz, PCO). – $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 101.0$ s. – $\text{C}_{16}\text{H}_{26}\text{F}_3\text{N}_2\text{O}_4\text{PSSi}$ (458.51): calcd. C 41.91, H 5.72, N 6.11; found C 40.14, H 5.55, N 6.59.

***t*BuC[OB(C₆F₅)₃]=PC(NMe₂)₂ (**6a**):** A 10% solution of tris(pentafluorophenyl)borane (5.52 g, 1.08 mmol) in toluene was added dropwise to a chilled solution (-30°C) of **2a** (0.23 g, 1.08 mmol) in toluene (40 mL). The mixture was slowly warmed to room temp., whereupon the slow formation of a precipitate occurred. After 3 h of stirring the bright yellow solid was filtered and washed with 5 mL of *n*-pentane. Yield: 0.52 g (66%) of yellow **6a**. – ^1H NMR (CD_2Cl_2): $\delta = 1.13$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 3.13 (s, 12 H, NCH_3). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 28.8$ [s, $\text{C}(\text{CH}_3)_3$], 45.4 (s, NCH_3), 48.4 [s, $\text{C}(\text{CH}_3)_3$], 137.0 (d, $J_{\text{CF}} = 247.7$ Hz, aryl-C), 139.5 (d, $J_{\text{CF}} = 247.2$ Hz, aryl-C), 147.5 (d, $J_{\text{CF}} = 237.9$ Hz, aryl-C), 147.9 (d, $J_{\text{CF}} = 240.1$ Hz, aryl-C), 188.5 (d, $J_{\text{CP}} = 89.0$ Hz, CN_2), 228.8 (d, $J_{\text{CP}} = 81.4$ Hz, PCO). – $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 68.3$ s. – $\text{C}_{28}\text{H}_{21}\text{BF}_{15}\text{N}_2\text{OP}$ (728.24): calcd. C 46.18, H 2.91, N 3.85; found C 46.16, H 3.03, N 3.81.

PhC[OB(C₆F₅)₃]=PC(NMe₂)₂ (6b**):** A 10% solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (6.56 g, 1.28 mmol) in toluene was added dropwise at room temp.

to a solution of **2b** (0.30 g, 1.28 mmol) in toluene (40 mL). After 30 min of stirring the formation of a yellow precipitate began. After 3 h the precipitate was filtered and washed with *n*-pentane (5 mL) to yield 0.72 g (75%) of **6b** as a yellow solid. – ^1H NMR (CD_2Cl_2): $\delta = 2.86$ (s, 12 H, NCH_3), 7.31 (m, 3 H, PhH), 7.39 (m, 2 H, PhH). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 44.6$ (s, NCH_3), 127.4 (s, PhC), 128.9 (s, PhC), 131.2 (s, PhC), 137.0 (d, $J_{\text{CF}} = 245.8$ Hz, aryl-C), 139.8 (d, $J_{\text{CF}} = 246.9$ Hz, aryl-C), 140.0 (s, PhC), 148.3 (d, $J_{\text{CF}} = 238.0$ Hz, aryl-C), 148.6 (d, $J_{\text{CF}} = 239.1$ Hz, aryl-C), 190.9 (d, $J_{\text{CP}} = 80.6$ Hz, CN_2), 223.4 (d, $J_{\text{CP}} = 71.9$ Hz, PCO). – $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 72.6$ (s). – $\text{C}_{30}\text{H}_{17}\text{BF}_{15}\text{N}_2\text{OP}$ (728.23): calcd. C 48.16, H 2.29, N 3.74; found C 48.12, H 2.08, N 3.73.

t*BuC[OAl(*t*Bu)₂Cl]=PC(NMe₂)₂ (**7a**):** 15.7 mL of a 0.1M solution of *t*Bu₂AlCl in toluene (1.57 mmol) was added dropwise at -40°C to a freshly prepared solution of **2a** (0.37 g, 1.57 mmol) in 40 mL of toluene. While warming to room temp. the color of the solution changed from yellow to orange. After 1 h of stirring the solvent was removed in vacuo and the oily residue was extracted with *n*-pentane (5×10 mL) to give **7a** as an orange, very moisture- and air-sensitive solid. Attempts to crystallize **7a** led to dismutation. A few crystals of *t*BuC[OAl(*t*Bu)₂Cl]=PC(NMe₂)₂ (**7a) were obtained after storing a solution of pure **7a** in C_6D_6 at $+6^{\circ}\text{C}$ for 3 weeks. – **7a**: ^1H NMR (C_6D_6): $\delta = 1.34$ [s, 9 H, $(\text{CH}_3)_3\text{CC}$], 1.38 [s, 18 H, $(\text{CH}_3)_3\text{CAl}$], 2.63 (s, 12 H, NCH_3). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 29.4$ [s, $\text{CC}(\text{CH}_3)_3$], 31.6 [s, $\text{AlC}(\text{CH}_3)_3$], 44.2 (s, NCH_3), 46.3 [d, $J_{\text{PC}} = 35.5$ Hz, $\text{CC}(\text{CH}_3)_3$], 184.4 (d, $J_{\text{PC}} = 76.5$ Hz, CN_2), 233.8 (d, $J_{\text{PC}} = 86.5$ Hz, PCO), the signal of $\text{AlC}(\text{CH}_3)_3$ was not detectable. – $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 72.9$ (s). – $\text{C}_{18}\text{H}_{39}\text{AlClN}_2\text{OP}$ (392.92): calcd. C 55.02, H 10.01, N 7.13; found C 54.89, H 10.13, N 7.05. – **7a***: $\text{C}_{14}\text{H}_{30}\text{AlCl}_2\text{N}_2\text{OP}$ (371.26): calcd. C 45.29, H 8.14, N 7.55; found 45.27, H 8.16, N 7.36.

PhC[OAl(*t*Bu)₂Cl]=PC(NMe₂)₂ (7b**):** Analogously, reaction of **2b** (0.34 g, 1.42 mmol) and *t*Bu₂AlCl (14.2 mL of a 0.1M solution in toluene, 1.42 mmol) in 40 mL of toluene led to the orange solid **7b** (0.38 g, 64%). Attempts to grow single crystals of **7b** from C_6D_6 at 6°C resulted in a dismutation and the isolation of a few crystals of $\text{PhC[OAl(*t*Bu)₂Cl]=PC(NMe₂)₂ (**7b***)}$ after 2 weeks. – **7b**: ^1H NMR (C_6D_6): $\delta = 1.37$ [s, 18 H, $\text{C}(\text{CH}_3)_3$], 2.63 (s, 12 H, NCH_3), 7.09 (m, 3 H, PhH), 8.07 (m, 2 H, PhH). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 29.7$ [s, $\text{C}(\text{CH}_3)_3$], 31.3 [s, $\text{C}(\text{CH}_3)_3$], 44.1 (s, NCH_3), 125.5 s, 128.7 s, 131.7 s, 143.5 (d, $J_{\text{PC}} = 39.0$ Hz, PhC), 185.3 (d, $J_{\text{PC}} = 71.8$ Hz, CN_2), 220.3 (d, $J_{\text{PC}} = 69.8$ Hz, PCO). – $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 78.2$ (s). – $\text{C}_{20}\text{H}_{35}\text{AlClOP}$ (412.92): calcd. C 58.18, H 8.54, N 7.78; found C 57.50, H 8.04, N 8.20.

***t*BuC(OAlMe₃)=PC(NMe₂)₂ (**8a**):** At -30°C 13.2 mL of a 0.1M solution of AlMe_3 in *n*-hexane (1.32 mmol) was added dropwise to a solution of **2a** (0.29 g, 1.32 mmol) in *n*-pentane (40 mL). The yellow color of the solution faded rapidly as it warmed up. The solvent was then removed in vacuo to leave **8a** as a pale-yellow very air- and moisture-sensitive oil. – ^1H NMR (C_6D_6): $\delta = -0.37$ (s, 9H, AlCH_3), 1.39 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.50 (s, 12 H, NCH_3). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = -5.2$ (s, AlCH_3), 28.5 [s, $\text{C}(\text{CH}_3)_3$], 43.6 (s, NCH_3), 46.3 [d, $J_{\text{CP}} = 34.7$ Hz, $\text{C}(\text{CH}_3)_3$], 189.9 (d, $J_{\text{CP}} = 78.3$ Hz, CN_2), 239.6 (d, $J_{\text{CP}} = 86.4$ Hz, PCO). – $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 62.7$ (s). – $\text{C}_{13}\text{H}_{30}\text{AlN}_2\text{OP}$ (288.41): calcd. C 54.14, H 10.48, N 9.71; found C 53.48, H 10.42, N 9.49.

PhC(OAlMe₃)=PC(NMe₂)₂ (8b**):** Similarly, 0.31 g (90%) of **8b** was obtained as an orange air- and moisture-sensitive oil from 1.12 mmol of AlMe_3 and 0.26 g (1.12 mmol) of **2b**. – ^1H NMR (C_6D_6): $\delta = -0.33$ (s, 9H, AlCH_3), 2.47 (s, 12H, NCH_3), 7.12 (m, 3H, PhH), 8.23 (m, 2H, PhH). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta =$

–5.7 (s, AlCH₃), 43.5 (s, NCH₃), 125.6 (s, PhC), 131.7 (s, PhC), 143.0 (d, ²J_{CP} = 40.4 Hz, *i*-PhC), 189.9 (d, ¹J_{CP} = 76.3 Hz, CN₂), 223.5 (d, ¹J_{CP} = 73.4 Hz, PCO). – ³¹P{¹H} NMR (CD₂Cl₂): δ = 64.9 s. – C₁₅H₂₆N₂AlOP (308.40): calcd. C 58.42, H 8.50, N 9.08; due to the extreme sensibility of **8b** no reliable elemental analyses could be obtained.

rBuC(O)PC(NMe₂)₂·GaMe₃ (9a): At –30 °C 11.5 mL of a 0.1 M solution of GaMe₃ in *n*-hexane (1.15 mmol) was added dropwise to a solution of **2a** (0.25 g, 1.15 mmol) in *n*-pentane (40 mL). After warm up to ambient temp. the solvent was carefully removed in vacuo to afford **9a** (0.32 g, 84%) as a yellow, very moisture- and air-sensitive oil. In vacuo (10^{–3} Torr) the adduct can be liberated completely from GaMe₃. – ¹H NMR (C₆D₆): δ = 0.08 (s, 9 H, GaCH₃), 1.37 [s, 9 H, C(CH₃)₃], 2.46 (s, 12 H, NCH₃). – ¹³C{¹H} NMR (CD₂Cl₂): δ = –2.0 (s, GaCH₃), 28.2 [s, C(CH₃)₃], 42.9 (s, NCH₃), 47.1 [d, J_{CP} = 38.6 Hz, C(CH₃)₃], 195.6 (d, J_{CP} = 76.3 Hz, CN₂), 237.3 (d, J_{CP} = 88.8 Hz, PCO). – ³¹P{¹H} NMR (CD₂Cl₂): δ = 38.7 (s, br). – C₁₃H₃₀GaN₂OP (331.09): calcd. C 47.16, H 9.13, N 8.46; found C 45.21, H 8.52, N 8.06.

rBuC(O)PC(NMe₂)₂·2GaMe₃ (10a): Analogously, 23.0 mL (2.30 mmol) of a 0.1 M solution of GaMe₃ in *n*-hexane was reacted with 0.25 g (1.15 mmol) of **2a** in 40 mL of *n*-pentane. After warming to room temp. the mixture was concentrated to 2 mL and stored at –30 °C for 24 h, whereupon yellow crystalline **10** (0.24 g, 63%) separated. The air- and moisture-sensitive adduct can be freed from GaMe₃ in vacuo. The chemical shifts in the NMR spectra of **10a** are essentially the same as of **9a** – a phenomenon, which is presumably caused by dissociation.

PhC(O)PC(NMe₂)₂·GaMe₃ (9b): A 0.1 M solution of GaMe₃ in *n*-hexane (7.8 mL, 0.78 mmol) was added dropwise to a cooled solution of **2b** (0.18 g, 0.78 mmol) in *n*-pentane (40 mL). After warming to ambient temp. the solvent was carefully removed in vacuo. Adduct **9b** (0.25 g, 91% yield) was obtained as an extremely air- and moisture-sensitive residue. Continued evacuation led to a complete removal of GaMe₃. – ¹H NMR (C₆D₆): δ = 0.05 (s, 9 H, GaCH₃), 2.47 (s, 12 H, NCH₃), 7.13 (m, 3 H, PhH), 8.19 (m, 2 H, PhH). – ¹³C{¹H} NMR (CD₂Cl₂): δ = –2.2 (s, GaCH₃), 43.1 (s, NCH₃), 126.7 s, 126.8 s, 133.0 s, 144.3 (d, J_{CP} = 43.9 Hz, PhC), 194.0 (d, J_{CP} = 79.5 Hz, CN₂), 225.4 (d, J_{PC} = 76.7 Hz, PCO). – ³¹P{¹H} NMR (CD₂Cl₂): δ = 48.1 (s, br). – C₁₅H₂₆GaN₂OP (351.08): calcd. C 51.32, H 7.46, N 7.98; found C 49.80, H 7.52, N 7.75.

rBuC(O)P(InMe₃)C(NMe₂)₂ (11a): Analogously, a 0.1 M solution of InMe₃ in *n*-hexane (9.6 mL, 0.96 mmol) was added at –40 °C dropwise to a solution of **2a** (0.21 g, 0.96 mmol) in 40 mL of *n*-pentane. The mixture was slowly warmed up to room temp. and the solvent was carefully removed in vacuo. Crude adduct **11a** was obtained as a yellow oily residue, which was redissolved in *n*-pentane (5 mL) and stored at –30 °C. Pure **11a** was isolated as orange crystals (0.29 g, 80%). – IR (KBr): $\tilde{\nu}$ = 1594 (s, CO), 1546 (s, CO) cm^{–1}. – ¹H NMR (C₆D₆): δ = 0.09 (s, br, 9 H, InCH₃), 1.36 [s, 9 H, C(CH₃)₃], 2.45 (s, 12 H, NCH₃). – ¹³C{¹H} NMR (CD₂Cl₂): δ = –4.6 (s, InCH₃), 27.9 [s, C(CH₃)₃], 43.1 (s, NCH₃), 47.7 [d, J_{CP} = 39.8 Hz, C(CH₃)₃], 195.5 (d, J_{CP} = 68.4 Hz, CN₂), 234.0 (d, J_{CP} = 84.5 Hz, PCO). – ³¹P{¹H} NMR (CD₂Cl₂): δ = 15.6 (s, br). – C₁₃H₃₀InN₂OP (376.18): calcd. C 41.51, H 8.04, N 7.45; found C 41.16, H 8.21, N 7.41.

PhC(O)P(InMe₃)C(NMe₂)₂ (11b): Adduct **11b** (0.40 g, 91%) was isolated as an air- and moisture-sensitive solid from the reaction of InMe₃ (1.12 mmol of a 0.1 M solution in *n*-hexane, 11.2 mL) and **2b** (0.28 g, 1.12 mmol) in 40 mL of *n*-pentane at –30 °C and after an analogous workup. – IR (KBr): $\tilde{\nu}$ = 1597 (sh, CO), 1540 (m, CO) cm^{–1}. – ¹H NMR (C₆D₆): δ = 0.06 (s, br, 9 H, InCH₃), 2.53

(s, 12 H, NCH₃), 7.13 (m, 3 H, PhH), 8.26 (m, 2 H, PhH). – ¹³C{¹H} NMR (CD₂Cl₂): δ = –4.7 (s, InCH₃), 42.2 (s, NCH₃), 126.4 s, 131.1 s, 133.0 s, 144.6 (d, J_{CP} = 46.7 Hz, PhC), 196.2 (d, J_{CP} = 76.6 Hz, CN₂), 219.9 (d, J_{CP} = 76.7 Hz, PCO). – ³¹P{¹H} NMR (CD₂Cl₂): δ = 36.8 (s). – C₁₅H₂₆InN₂OP (396.17): calcd. C 45.48, H 6.61, N 7.07; found C 44.27, H 6.56; N 6.65.

[rBuC(O)P{Cr(CO)₅}C(NMe₂)₂] (12a): A solution of [{(Z)-cyclooctene}Cr(CO)₅] (0.33 g, 1.08 mmol) in 10 mL of diethyl ether was added dropwise to a chilled solution (–30 °C) of 1.08 mmol of **2a**, prepared in situ from 0.13 g of pivaloyl chloride and 0.22 g of **1**, in 40 mL of diethyl ether. The solution was warmed to room temp. and was stirred for 2 h. Evaporation to dryness afforded **12a** as a yellow solid, which was crystallized from toluene at –30 °C (Yield 0.35 g, 79%). – IR (KBr): $\tilde{\nu}$ = 2051 [m, (CrCO)], 1987 [m, (CrCO)], 1919 [s, (CrCO)], 1900 [s, (CrCO)], 1584 [m, (CO)_{acyl}], 1553 [m, (CO)_{acyl}] cm^{–1}. – ¹H NMR (C₆D₆): δ = 1.34 [s, 9 H, C(CH₃)₃], 2.42 (s, br, 12 H, NCH₃). – ¹³C{¹H} NMR (C₆D₆): δ = 27.9 [s, C(CH₃)₃], 43.2 [s, NCH₃], 48.4 [d, J_{PC} = 40.8 Hz, C(CH₃)₃], 198.7 (d, J_{PC} = 48.0 Hz, CN₂), 218.2 (s, CrCO_{eq}), 225.1 (s, CrCO_{ax}), 235.3 (d, J_{PC} = 75.2 Hz, PCO). – ³¹P{¹H} NMR (C₆D₆): δ = –12.8 (s). – C₁₅H₂₁CrN₂O₆P (408.31): calcd. C 44.12, H 5.18, N 6.86; found: C 44.10, H 4.93, N 6.78.

[PhC(O)P{Cr(CO)₅}C(NMe₂)₂] (12b): A solution of [{(Z)-cyclooctene}Cr(CO)₅] (0.43 g, 1.42 mmol) in *n*-pentane (10 mL) was added dropwise to a chilled solution (–40 °C) of **2b**, prepared in situ from 0.29 g (1.42 mmol) of **1** and 0.20 g (1.42 mmol) of benzoyl chloride, in 40 mL of *n*-pentane. The suspension was slowly warmed to room temp. whereupon its color changed from yellow to orange-red. Solvent and volatile components were removed in vacuo, and the residue was washed with cold *n*-pentane (2 × 10 mL, –30 °C) to afford 0.43 g (71% yield) of **12b** as an orange-red microcrystalline solid. – IR (KBr): $\tilde{\nu}$ = 2051 [vs, (CrCO)], 1929 [vs, (CrCO)], 1900 [vs, (CrCO)], 1564 [sh, (CO)_{acyl}], 1545 [m, (CO)_{acyl}] cm^{–1}. – ¹H NMR (CD₂Cl₂): δ = 3.01 (s, 12 H, NCH₃), 7.42 (m, 2 H, PhH), 7.48 (m, 1 H, PhH), 7.68 (m, 2 H, PhH). – ¹³C{¹H} NMR (CD₂Cl₂): δ = 43.8 (s, NCH₃), 127.4 s, 128.6 s, 132.0 s, 142.7 (d, J_{CP} = 12.6 Hz, PhC), 202.0 (d, J_{CP} = 52.3 Hz, CN₂), 218.2 [s, Cr(CO)_{eq}], 222.0 (d, J_{CP} = 40.6 Hz, PCO), 225.4 [s, Cr(CO)_{ax}]. – ³¹P{¹H} NMR (CD₂Cl₂): δ = 1.9 (s). – C₁₇H₁₇CrN₂O₆P (428.30): calcd. C 47.67, H 4.00, 6.54; found C 47.64, H 4.08, N 6.46.

[rBuC(O)P{Fe(CO)₄}C(NMe₂)₂] (13a): Solid [Fe₂(CO)₉] (0.50 g, 1.37 mmol) was added to a solution of 1.37 mmol of **2a**, prepared in situ from **1** (0.28 g) and pivaloyl chloride (0.17 g), in 40 mL of diethyl ether at –30 °C. The mixture was allowed to warm to ambient temp. and stirring was continued for 18 h. The solution changed color from orange to red. It was evaporated to dryness to give **13a** as a red powder, which was crystallized from diethyl ether at –30 °C. (Yield: 0.38 g, 73%). – IR (KBr): $\tilde{\nu}$ = 2028 [s, (FeCO)], 1943 [s, (FeCO)], 1927 [s, (FeCO)], 1596 [s, (CO)_{acyl}], 1560 [m, (CO)_{acyl}] cm^{–1}. – ¹H NMR (C₆D₆): δ = 1.41 [s, 9 H, C(CH₃)₃], 2.43 (s, 12 H, NCH₃). – ¹³C{¹H} NMR (C₆D₆): δ = 28.0 [s, C(CH₃)₃], 43.3 (s, NCH₃), 49.0 [d, J_{PC} = 42.0 Hz, C(CH₃)₃], 195.2 (d, J_{PC} = 55.4 Hz, CN₂), 217.0 (s, FeCO), 235.3 (d, J_{PC} = 80.0 Hz, PCO). – ³¹P{¹H} NMR (C₆D₆): δ = –26.4 (s). – C₁₅H₂₁FeN₂O₅P (384.15): calcd. C 43.77, H 5.51, N 7.29; found C 43.65, H 5.60, N 7.23.

[PhC(O)P{Fe(CO)₄}C(NMe₂)₂] (13b): Analogously, red microcrystalline **13b** (0.48 g, 76% yield) was prepared from 1.57 mmol of **2b**, obtained in situ from **1** (0.32 g) and benzoyl chloride (0.22 g), and 0.57 g (1.57 mmol) of [Fe₂(CO)₉] in 40 mL of diethyl ether at room temp. over a period of 20 h. – IR (KBr): $\tilde{\nu}$ = 2031 [s, (FeCO)],

Table 2. Crystallographic data for **6b**, **7b***, **10a**, **11a** and **12a**

	6b	7b*	10a	11a	12a
formula	C ₃₀ H ₁₇ BF ₁₅ N ₂ OP	C ₁₆ H ₂₆ AlCl ₂ N ₂ OP	C ₁₆ H ₃₉ Ga ₂ N ₂ OP	C ₁₃ H ₃₀ InN ₂ OP	C ₁₅ H ₂₁ CrN ₂ O ₆ P
color	yellow	yellow	yellow	yellow	yellow
size (mm ³)	0.68 × 0.53 × 0.16	1.1 × 0.6 × 0.3	1.2 × 0.8 × 0.5	0.7 × 0.5 × 0.2	0.8 × 0.4 × 0.4
<i>M_r</i>	748.24	391.24	445.90	376.18	408.31
space group	<i>Pbca</i>	<i>P1</i>	<i>P1</i>	<i>P1</i>	<i>P1</i>
<i>a</i> (Å)	18.8661(3)	10.071(4)	9.651(5)	9.712(8)	9.500(3)
<i>b</i> (Å)	14.1381(3)	10.665(2)	10.259(7)	10.076(10)	9.738(3)
<i>c</i> (Å)	23.9734(5)	10.635(5)	12.758(7)	10.033(7)	11.394(3)
α (°)		82.51(3)	85.64(5)	96.11(7)	80.36(2)
β (°)		68.94(3)	74.57(4)	94.70(6)	86.83(3)
γ (°)		76.47(2)	70.61(5)	105.85(7)	68.82(2)
<i>V</i> (Å ³)	6394.4(2)	1035.0(7)	1148.5(12)	932.8(14)	969.0(5)
ρ_{calcd} (g cm ⁻³)	1.554	1.255	1.289	1.339	1.399
<i>Z</i>	8	2	2	2	2
<i>F</i> (000)	2992	412	468	388	424
μ (mm ⁻¹)	0.202	0.438	2.419	1.347	0.704
2θ range (°)	4.0 < 2θ < 56.6	4.0 < 2θ < 60.0	4.0 < 2θ < 60.0	4.0 < 2θ < 50.0	3.0 < 2θ < 60.0
<i>T</i> (K)	293	173	173	173	173
refl. measured	53084	6335	7053	3501	6147
unique refl.	6436	6020	6685	3281	5645
abs. refl. (<i>I</i>) > 2 σ (<i>I</i>)	4316	4507	5227	2321	4530
parameters	451	215	212	173	233
max. resid. dens., e Å ⁻³	0.44	0.34	0.86	1.16	0.32
<i>R</i> ₁ ^[a]	0.062	0.044	0.044	0.068	0.038
<i>wR</i> ₂ ^[a]	0.146	0.114	0.107	0.172	0.091

^[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$; *R*₁ for abs. data, weighted for all data on *F*².

1913 [vs. (FeCO)], 1603 [s, (CO)_{acyl}], 1550 [m, (CO)_{acyl}] cm⁻¹. – ¹H NMR (C₆D₆): δ = 2.41 (s, 12 H, NCH₃), 7.13 (m, 3 H, PhH), 8.03 (m, 2 H, PhH). – ¹³C{¹H} NMR (C₆D₆): δ = 43.9 (s, NCH₃), 127.8 (s), 128.6 (s), 132.2 (s), 141.6 (d, *J*_{CP} = 43.9 Hz, PhC), 195.6 (d, *J*_{CP} = 56.1 Hz, CN₂), 216.2 (s, FeCO), 221.9 (d, *J*_{CP} = 56.5 Hz, PCO). – ³¹P{¹H} NMR (C₆D₆): δ = -13.6 (s). – C₁₆H₁₁FeN₂O₅P (404.14): calcd. C 47.55, H 4.24, N 6.93; found C 47.52, H 4.08, N 6.54.

[rBuC(O)P{Ni(CO)₃}C(NMe₂)₂] (14a): A solution of [Ni(CO)₄] (0.23 g, 1.37 mmol) in 10 mL of diethyl ether was added dropwise to the chilled solution (-30°C) of 1.37 mmol **2a**, prepared from 0.28 g **1** and 0.17 g of pivaloyl chloride, in diethyl ether (30 mL). The mixture was allowed to warm to room temp. and was stirred for 1 h, whereupon its color changed from orange to red-brown. Volatile components were removed in vacuo, and the red solid residue was washed with 20 mL of cold *n*-pentane (-30°C). Recrystallization from diethyl ether afforded orange crystalline **14a** (0.26 g, 50%). Upon exposure to daylight, the crystals turned brown rapidly. – IR (KB): $\tilde{\nu}$ = 2054 [s, (NiCO)], 1976 [s, (NiCO)], 1966 [s, (NiCO)], 1584 [s, (CO)_{acyl}], 1542 [m, (CO)_{acyl}] cm⁻¹. – ¹H NMR (C₆D₆): δ = 1.38 [s, 9 H, C(CH₃)₃], 2.53 (s, 12 H, NCH₃). – ¹³C{¹H} NMR (C₆D₆): δ = 27.6 [s, C(CH₃)₃], 42.5 (s, NCH₃), 48.1 [d, *J*_{PC} = 41.5 Hz; C(CH₃)₃], 196.7 (s, NiCO), 198.4 (d, *J*_{PC} = 48.9 Hz, CN₂), 232.2 (d, *J*_{PC} = 70.6 Hz, PCO). – ³¹P{¹H} NMR (C₆D₆): δ = -11.7 (s). – C₁₃H₂₁N₂NiO₄P (358.99): calcd. C 43.50, H 5.90, N 7.80; found C 43.47, H 5.80, N 7.79.

X-ray Crystallography: Data collection for **6b** was performed on a 1 K-Siemens (Bruker) AXS-CCD-diffractometer using omega-scan techniques; integration and absorption correction with Siemens-Saint program, structure solution with direct methods and refinement on *F*² with Siemens SHELXTL Vers. 5.03 with riding models for hydrogen atoms.

For **7b***, **10a**, **11a** and **12a** crystallographic data (Table 2) were collected with a Siemens P2₁ four-circle diffractometer using graphite-monochromated Mo-*K*_α radiation. Semi-empirical absorption cor-

rections using ψ -scans were applied. Crystallographic programs used for structure solutions and refinements were SHELXTL PLUS and SHELXL-97. The structures were solved by direct methods and refined by using full-matrix least squares on *F*² and all unique reflections and attributing anisotropic thermal parameters to all non-hydrogen atoms. Hydrogen atoms were included at calculated positions using a riding model.^[29] Crystal data collection and refinement parameters are given in Table 2. ORTEP drawings of the solid state structures of **6b**, **7b***, **10a**, **11a** and **12a** are shown in Figures 1–6. Bonding parameters are given in the captions and in Table 1.

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- [29] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC–135114 (**6b**), CCDC–134975 (**7b***), CCDC–134976 (**10a**), CCDC–134977 (**11a**) and CCDC–134978 (**12a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk].

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