

REACTIONS OF 1-ADAMANTYLPHOSPHINE AND BIS-(1-ADAMANTYL)PHOSPHINE WITH CARBONYLS OF GROUP 6, 8 AND 10 METALS. REACTIVITY OF THE P—H BOND IN 1-ADAMANTYLPHOSPHINE COMPLEXES*

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Abstract—The reactions between $(1\text{-Ad})_n\text{PH}_{3-n}$ (1-Ad = 1-adamantyl; $n = 1, 2$) and $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}; \text{Mo}, \text{W}$), $\text{Fe}_2(\text{CO})_9$ and $\text{Ni}(\text{CO})_4$ led to mononuclear derivatives of the type $(\text{OC})_m\text{M}[(1\text{-Ad})_n\text{PH}_{3-n}]$ ($m = 5, \text{M} = \text{Cr}, \text{Mo}, \text{W}; m = 4, \text{M} = \text{Fe}; m = 3, \text{M} = \text{Ni}; n = 1, 2$). Although rather unreactive, as a result of the 1-adamantyl substitution, some of these compounds were employed for further synthesis under more vigorous conditions. Thus, pyrolysis of $(1\text{-AdPH}_2)_2\text{Fe}(\text{CO})_4$ (7) furnished the binuclear cluster $(1\text{-AdPH})_2\text{Fe}_2(\text{CO})_6$ (11), whereas substitution of a PH proton in the chromium complex $(1\text{-AdPH}_2)\text{Cr}(\text{CO})_5$ (1) by a diisopropylphosphino group led to the diphosphine complex $(\text{OC})_5\text{Cr}(1\text{-AdPH}-\text{P}^i\text{Pr}_2)$ (15), which isomerized at elevated temperatures to $(1\text{-AdPH}-\text{P}^i\text{Pr}_2)\text{Cr}(\text{CO})_5$ (15a) with liberation of the diphosphine $1\text{-AdPH}-\text{P}^i\text{Pr}_2$ (16). The crystal structure of 15 is described; the P—P bond length is 223.6(1) pm. 1-AdPH_2 reacted with $\text{Fe}_3(\text{CO})_{12}$ with the formation of a mixture of bi- and trinuclear iron carbonyl clusters.

Primary and secondary phosphines resemble the majority of phosphorus(III) compounds in that they react with metal carbonyls, substituting carbon monoxide.¹ As a result of the reactivity of the —PH₂ or the —PH group these compounds can serve as versatile precursors in the synthesis of new compounds. The synthesis of species that are unknown or unstable in an uncoordinated state may be realized in the coordination sphere of a transition metal. Thus, based on phosphine complexes, Treichel and his co-workers²⁻⁴ have described the synthesis of phosphido complexes; Stelzer and his co-workers⁵ have synthesized di-, tri- and tetraphosphines coordinated to metal carbonyl fragments; Mathey and his co-workers⁶⁻⁹ have reported the synthesis of phosphalkene and phosphirane complexes from coordinated phosphine

precursors. Complexes involving PH phosphines have also been used in the synthesis of oligonuclear transition metal clusters.^{10,11}

A variety of metal complexes involving primary and secondary phosphines as ligands are known, but the substituents were always aromatic or sterically undemanding alkyl groups. In the course of our studies on tertiary, bulky hydrocarbon group substituents at phosphorus¹²⁻¹⁴ the question arose whether the comparatively unreactive 1-adamantyl-substituted phosphines of the type $(1\text{-Ad})_n\text{PH}_{3-n}$ ($n = 1, 2$) could be employed as ligands and, if so, whether further chemical reactions at the coordinated phosphine ligands would be possible.

RESULTS AND DISCUSSION

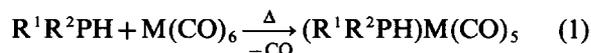
Reactions of 1-adamantylphosphine and bis-(1-adamantyl)phosphine with carbonyls of group 6, 8 and 10 metals

* Dedicated to Professor R. W. Parry on the occasion of his 75th birthday.

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The reaction of 1-adamantyl- and bis-(1-adamantyl)phosphine with a slight excess of the hexa-

carbonyls of chromium(0), molybdenum(0) and tungsten(0) in high-boiling solvents at 110–140°C was found to lead, selectively, to the mono-substituted derivatives with the loss of carbon monoxide [eq. (1)]. Reactivities and yields were found to decrease from chromium to tungsten carbonyl.



R ¹	R ²	Cr	Mo	W
1-Ad	H	1	2	3
1-Ad	1-Ad	4	5	6

Products 1–6 are colourless solids that are stable in air for hours. They may be purified by re-

crystallization from THF. The $\delta(^{31}\text{P})$ values of 1–6 exhibit a significant low-field shift from those of the starting phosphines [1-AdPH₂, –81.6 ppm and (1-Ad)₂PH, 18.71 ppm] (Table 1).

The deshielding effect increases from the tungsten to the chromium complexes. This could be a result of the decrease in the number of electrons at the metal atom and, consequently, a weakened shielding effect. In the ¹H NMR spectra of 1–6, besides the signals due to the 1-adamantyl groups, the resonances of the phosphine protons are observed in the region 3.81–4.08 ppm (Table 1). Both $\delta(^{31}\text{P})$ and ¹J(PH) (302.50–321.00 Hz)¹⁵ lie in the expected region. In the ¹³C NMR-spectra the *cis*- and *trans*-CO groups may be distinguished on the basis of

Table 1. ¹H, ³¹P NMR and IR data of compounds 1–10, 12 and 13

	δ_{P}	$\delta_{\text{H}}(\text{PH})$ ¹ J(PH) $\delta_{\text{H}}(\text{C}_{10}\text{H}_{15})$	IR (hexane) $\nu(\text{CO})$ $\nu(\text{PH})$
(1-AdPH ₂)Cr(CO) ₅ 1	0.54	4.04 312.81 1.71–2.03	2066(s), 1985(s), 1945(vs) 2315(w)
(1-AdPH ₂)Mo(CO) ₅ 2	–28.51	4.08 308.16 1.66–2.06	2074(s), 1987(m), 1952(vs) 2317(w)
(1-AdPH ₂)W(CO) ₅ 3	–47.59 ¹ J(PW) = 212.53	4.44 321.00 1.66–2.07	2075(s), 1980(m), 1945(vs) 2321(vw)
(1-Ad ₂ PH)Cr(CO) ₅ 4	70.39	3.81 307.18 1.74–2.07	2058(m), 1985(s), 1937(vs) 2300(w)
(1-Ad ₂ PH)Mo(CO) ₅ 5	53.46	3.89 302.50 1.74–2.06	2069(s), 1978(m), 1941(vs) 2300(w)
(1-Ad ₂ PH)W(CO) ₅ 6	39.15 ¹ J(PW) = 216.15	4.21 314.32 1.73–2.07	2065(s), 1989(vs), 1934(vs) 2301(vw)
(1-AdPH ₂)Fe(CO) ₄ 7	14.03	4.65 343.69 1.75–2.09	2056(s), 1983(s), 1949(vs) 2325(w)
(1-Ad ₂ PH)Fe(CO) ₄ 8	81.83	3.98 328.04 1.72–2.02	2048(s), 1985(s), 1947(vs) 2310(w)
(1-AdP)Fe ₃ (CO) ₉ H ₂ 9	458.95	$\delta_{\text{H}}(\text{H}_2) = -24.09$ ² J(PH) = 27.41 1.95–2.18	2091(m), 2058(s), 2029(vs), 2003(s), 1983(m), 1974(w)
(1-AdP) ₂ Fe ₃ (CO) ₉ 10	400.85	1.77–2.13 3.85	2032(vs), 2013(vs), 1995(vs), 1984(s), 1970(w)
(1-AdPH ₂)Ni(CO) ₃ 12	–35.03	298.11 1.78–2.04	2075(s), 2002(vs), 2319(m)
(1-Ad ₂ PH)Ni(CO) ₃ 13	59.92	3.66 301.14 1.70–1.96	2064(s), 1990(vs), 2299(m)

Table 2. ¹³C NMR data of compounds 1–10, 12 and 13

	$\delta_c(C^1)$ $^1J(PC)$	$\delta_c(C^2)$ $^2J(PC)$	$\delta_c(C^3)$ $^3J(PC)$	$\delta_c(C^4)$ $^4J(PC)$	$\delta_c(CO)_{cis}^a$ $^2J(PC)$	$\delta_c(CO)_{trans}^a$ $^2J(PC)$
(1-AdPH ₂)Cr(CO) ₅	33.15	41.85	28.54	35.98	216.71	220.90
1	24.55	—	9.32	—	13.17	6.58
(1-AdPH ₂)Mo(CO) ₅	31.73	42.09	28.54	35.99	205.44	208.34
2	25.22	1.21	9.50	1.22	8.87	21.99
(1-AdPH ₂)W(CO) ₅	32.09	41.94	28.52	35.99	195.93	196.93
3	28.62	—	9.80	—	6.87	21.82
(1-Ad ₂ PH)Cr(CO) ₅	40.09	42.44	28.98	36.21	218.59	222.00
4	10.52	—	8.21	—	12.00	5.82
(1-Ad ₂ PH)Mo(CO) ₅	32.33	42.68	28.92	36.27	207.23	210.49
5	11.22	1.25	8.40	—	8.28	22.31
(1-Ad ₂ PH)W(CO) ₅	39.04	42.77	28.94	36.26	198.31	198.90
6	14.86	—	8.41	—	6.58	21.79
(1-AdPH ₂)Fe(CO) ₄	34.08	40.99	28.41	35.92	—	213.22
7	28.83	—	9.95	—	—	19.37
(1-Ad ₂ PH)Fe(CO) ₄	39.68	41.96	28.85	36.29	—	219.36
8	15.57	—	8.64	—	—	13.45
(1-AdP)Fe ₃ (CO) ₉ H ₂	47.55	36.12	29.44	44.70	—	208.34
9	6.81	1.93	10.42	—	—	—
(1-AdP) ₂ Fe ₃ (CO) ₉	48.94	35.93	29.80	43.20	—	213.90
10	^b —	^b —	^b —	^b —	—	—
(1-AdPH ₂)Ni(CO) ₃	29.98	42.12	28.56	36.17	—	195.98
12	24.97	2.00	9.35	—	—	—
(1-Ad ₂ PH)Ni(CO) ₃	36.32	42.04	28.72	36.51	—	197.47
13	12.92	2.82	8.46	—	—	—

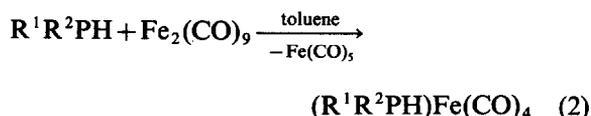
^a *Cis/trans* only for the octahedral complexes 1–6.

^b X-part of an ABX spectrum.

their $\delta(^{13}C)$ and $^2J(PC)$ values:¹⁶ the $\delta(^{13}C)$ values of *trans*-CO groups are observed consistently at lower field than those of the *cis*-CO groups. In the case of the molybdenum and tungsten complexes $^2J(PC)_{trans}$ is always larger than $^2J(PC)_{cis}$, while the opposite is true for the chromium complexes **1** and **4** (Table 2), in accord with expectation.¹⁶

Belonging to the point group C_{4v} , for complexes 1–6 in the IR spectra three IR-active bands are expected in the CO region¹⁷ and are indeed observed. $\nu(PH)$ is observed in all IR spectra in the region 2299–2321 cm^{-1} (Table 1).¹⁸ The mass spectra of 1–6 are found to exhibit the molecular ion peaks resulting from the successive loss of five CO groups and a peak at m/z 135 from the 1-adamantyl fragment. In the mass spectra of 4–6 signals from the free ligand, (1-Ad)₂PH, are observed.

The mononuclear derivatives of iron pentacarbonyl, **7** and **8**, were synthesized from (1-Ad)_nPH_{3-n} and Fe₂(CO)₉ in toluene as an inert solvent at room temperature [eq. (2)]. The products are orange-brown solids, melting with decomposition.



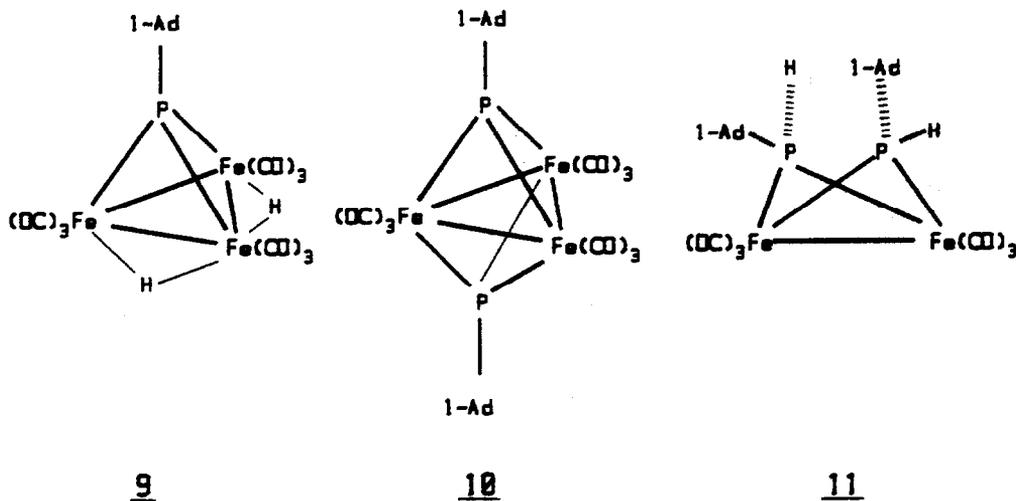
For **7** $\delta(^{31}P)$ is shifted by *ca* 86 ppm and for **8** by *ca* 64 ppm to high field, compared with the free ligands. The $\delta(^1H)$ and $^1J(PH)$ values of the phosphine protons are in accord with expectation and are closely similar to those of 1–6 (Table 1). In the ¹³C NMR spectra of both compounds only one resonance, a doublet due to ³¹P—¹³C coupling, is observed for the carbonyl groups (Table 2). Assuming trigonal-bipyramidal geometry at Fe(0) a pseudo-rotation process, too fast to be followed by ¹³C NMR spectroscopy, would account for this observation. The mass spectra of **7** and **8** exhibit the molecular ion with low intensity and the successive loss of the four carbonyl groups is seen. The IR spectra of **7** and **8** display the expected three bands in the carbonyl region, consistent with the

C_{3v} point group¹⁷ and $\nu(\text{PH})$ bands at 2325 (7) and 2310 cm^{-1} (8).

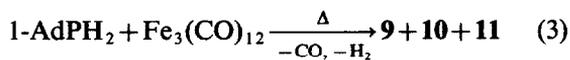
The reaction of primary phosphines with $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ has been studied.^{10,19,20} In all cases oligonuclear phosphinidene clusters were obtained. In the case of osmium the primary reaction product, $\text{Os}_3(\text{CO})_{11}(\text{RPH}_2)$ ($\text{R} = \text{Ph}$, $c\text{-C}_6\text{H}_{11}$) is well known.^{20,21} It was thus of interest to determine whether the comparatively unreactive 1-AdPH₂ would yield products analogous to the osmium complexes in its reaction with $\text{Fe}_3(\text{CO})_{12}$. Three signals in the ³¹P NMR spectra of the reaction mixture [$\delta(^{31}\text{P})$ 458.95, 400.85 and 150.88 in a 3:8:1 ratio] were assigned to the clusters **9**, **10** and **11**. These assignments are based on those of the

the resonance of the carbonyl groups, suggesting a dynamic structure. For the 1-adamantyl cage the expected four signals are observed, with an unusually small value for ¹J(PC) of 6.81 Hz, as against a larger ³J(PC) value of 10.42 Hz. The mass spectrum exhibits the molecular ion at m/z 588, fragments from the successive loss of nine carbonyl groups and the fragments $[\text{Fe}_3\text{PH}]^+$, $[\text{Fe}_3\text{P}]^+$ and $[\text{Ad}]^+$. The IR spectrum, similar to that of the analogous 'butyl compound,¹⁰ shows six bands in the carbonyl region, suggesting a similar structure.

A resonance, $\delta(^{31}\text{P}) = 400.85$ ppm, shifted by *ca* 5 ppm to high field, relative to the analogous 'butyl compound,²³ is observed for **10** in the region typical of μ^3 -phosphido ligands. Stelzer and his co-workers



analogous 'butyl-substituted compounds, from the work of Huttner,^{10,23} Vahrenkamp¹¹ and Stelzer²² [eq. (3)]. There was no evidence for a primary substitution product, $\text{Fe}_3(\text{CO})_{11}(1\text{-AdPH}_2)$. Of the three components of the reaction mixture **9** and **10** could be isolated in a pure state. The phosphido cluster (**11**), present here solely as one of the symmetric isomers, was subsequently synthesized by a different method (*vide infra*).



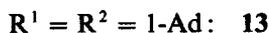
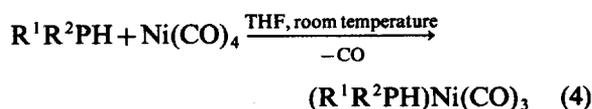
The singlet absorption at 458.95 ppm in the ³¹P NMR spectrum of **9** is typical of a μ^3 -phosphido ligand. Compared with the signal of the analogous 'butyl compound¹⁰ there is a high-field shift of *ca* 8 ppm. A difference of this magnitude in $\delta(^{31}\text{P})$ between analogous 'butyl- and 1-adamantylphosphorus compounds is almost always observed, irrespective of the coordination number of phosphorus.¹³ $\delta(^1\text{H})$ for the bridging hydrogen atoms is -24.09 ppm, with ²J(PH) = 27.41 Hz. In the ¹³C NMR spectra of **9** only one signal is observed for

have obtained such compounds as stable products of the thermally initiated reaction of primary phosphines with $\text{Fe}(\text{CO})_5$.²² The ¹³C NMR spectrum of **10** in the carbonyl region shows a single line for the carbonyl groups at 213.90 ppm. The ¹³C NMR resonances of the atoms C¹ and C³ of the 1-adamantyl cage appear as X parts of ABX spectra, as a result of coupling with the two non-equivalent phosphorus atoms of the molecule. The mass spectrum of **10** shows a low intensity molecular ion at m/z 752 and fragments originating from successive loss of the nine carbonyl groups. In addition, signals due to the fragments $[\text{Fe}_3\text{P}_2\text{Ad}]^+$, $[\text{Fe}_2\text{P}_2\text{Ad}]^+$, $[\text{Fe}_3\text{P}_2]^+$, $[\text{Fe}_3\text{P}]^+$ and $[\text{Ad}]^+$ are observed.

As for the analogous 'butyl compound²³ five bands are observed in the carbonyl region of the IR spectrum of **10**, their wave numbers differing only slightly from those of the 'butyl analogue. The number and position of these bands confirm the assumed structure.

For the synthesis of mononuclear nickel(0)-phosphine derivatives a large excess of $\text{Ni}(\text{CO})_4$ was added to solutions of the phosphines $(1\text{-Ad})_n\text{PH}_{3-n}$ ($n = 1, 2$) in THF. The reaction mixtures were

stirred at room temperature until the evolution of carbon monoxide ceased [eq. (4)].

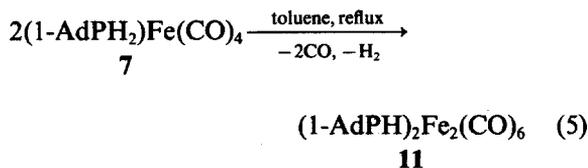


Compound **12** was obtained as a colourless oil, crystallizing at -18°C , while **13** was a colourless solid. As expected there is a marked low-field shift of $\delta(^{31}\text{P})$ (Table 1). In the ^1H NMR spectra signals typical of PH protons are observed at 3.85 (**12**) and 3.66 ppm (**13**), with $^1J(\text{PH}) = 298.11$ and 301.14 Hz, respectively (Table 1). In the ^{13}C NMR spectra of both complexes only single resonances are observed for the carbonyl groups. There is a conspicuous high field shift of the ^{13}C NMR resonances of the C¹ atoms of the 1-adamantyl group. In the mass spectrum of **12** the molecular ion is seen at m/z 310, whereas for **13** the heaviest fragment arises from the loss of one carbonyl group from the parent molecule. Further characteristic fragments are the result of the successive loss of carbon monoxide. The base peak, in both cases, is the adamantyl cation (m/z 135). The IR spectra (C_{3v}, molecular symmetry) reveal two bands¹⁷ in the carbonyl region, in agreement with reports on mononuclear nickel carbonyl complexes of other phosphines.²⁴ IR absorptions due to $\nu(\text{PH})$ are seen at 2319 (**12**) and 2299 cm^{-1} (**13**).¹⁸

Reactions of metal carbonyl-phosphine complexes

As mentioned above, we succeeded in isolating the two trinuclear iron(0) clusters **9** and **10** from the

reaction mixture of 1-AdPH₂ and Fe₃(CO)₁₂, whereas the isolation of a third product [$\delta(^{31}\text{P})$ 150.88] failed. Based on the comparison of the $\delta(^{31}\text{P})$ values to those of other, structurally analogous compounds,^{11,22} this signal is assigned to an isomer of the phosphido cluster (**11**). In order to ascertain its identity an alternative synthesis of **11** was realized, following a previously reported procedure,¹¹ by refluxing a solution of the phosphine complex **7** in toluene [eq. (5)]. A 1 : 1 ratio of **7** : **11** was determined (^{31}P NMR) after a 6 h reflux period.



This ratio remained unchanged upon continued refluxing. Upon work-up by column chromatography **11** was obtained as a yellow solid, consisting of a 1 : 1 mixture of the isomers **11a** and **11b**. From the $\delta(^{31}\text{P})$ value of **11a** (150.88 ppm) it was concluded that it was one of the products obtained in the reaction of 1-AdPH₂ with Fe₃(CO)₁₂. The ^{31}P NMR spectrum of **11b**, due to the non-equivalence of the two phosphorus atoms, shows a higher order AB type NMR pattern. Presumably as a result of the steric demand of the bulky 1-adamantyl group, isomer **11c** is not observed (Fig. 1).

In contrast, Stelzer and his co-workers obtained a mixture of all three possible isomers²² from the reaction of Fe(CO)₅ with PhPH₂, presumably because of the lower steric demand of the phenyl group. The ^1H NMR spectrum of our mixture of isomers, **11a** and **11b**, is found to exhibit numerous lines in the region 2.81–5.15 ppm, which originate

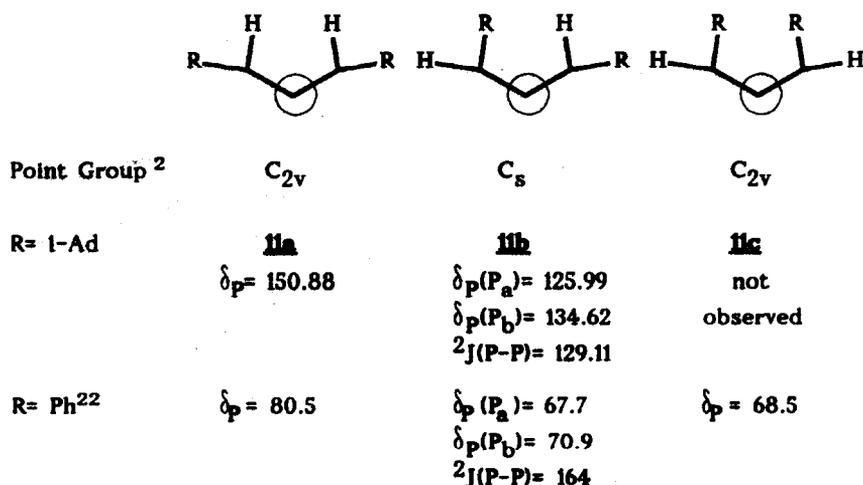


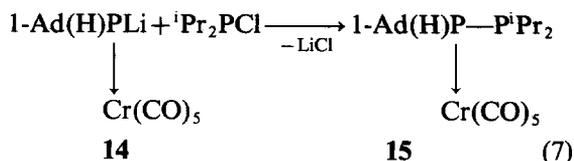
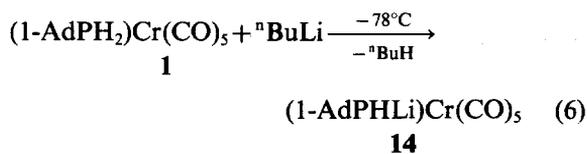
Fig. 1. Newman projection of compounds **11a**, **11b** and **11c**.

from the higher order spectra to be expected for the protons of the phosphido bridges. A precise assignment of the partially overlapping signals was unsuccessful. The mass spectrum of **11a/11b** shows the molecular ion at m/z 614, fragments originating from the successive loss of six CO groups and the ions $[\text{Fe}_2\text{P}_2]^+$ and $[\text{Ad}]^+$. Four bands are observed in the carbonyl region of the IR spectrum; they are shifted to slightly lower wave numbers than those of the analogous ¹butyl compound.

The formation of heterometallic clusters in the reaction of coordinated phosphines with oligonuclear metal carbonyls has been described in the literature.^{10,11,25-27} Employing the conditions described by Huttner and his co-workers,¹⁰ an equimolar mixture of $\text{Fe}_3(\text{CO})_{12}$ and **1** in toluene was heated for 12 h at 80°C. An inspection by ³¹P NMR spectroscopy revealed only the signal of **1** and there was no indication of possible product signals²⁷ after another 3 h reflux period. The reason for the failure of this reaction under the conditions employed may be the comparatively low reactivity of 1-adamantyl-substituted phosphorus compounds.

In analogy to reports by Stelzer and his co-workers⁵ an attempt was made to substitute one or two of the phosphino protons in **2** by diphenylphosphino groups, forming coordinated di- or triphosphines. However, ³¹P NMR gave no evidence for any reaction, either after stirring a mixture of **2** and diphenylchlorophosphine in toluene in the presence of triethylamine for several days at room temperature or after a 5 h reflux period. The failure of the reaction, in contrast to the analogous reaction of the phenylphosphine-substituted molybdenum pentacarbonyl derivative, is again thought to be due to the reduced reactivity of the 1-adamantyl phosphine derivative **2**.

A successful attempt at the formation of a PP bond in the coordination sphere of a metal was based on the reaction of $(1\text{-AdPH}_2)\text{Cr}(\text{CO})_5$ (**1**) with *n*-butyl lithium, forming the yellow lithium phosphido complex **14**; subsequent addition of diisopropylchlorophosphine gave compound **15**, the chromium pentacarbonyl derivative of the unknown unsymmetrical diphosphine **16**, in high yield [eqs (6) and (7)]. The ³¹P NMR spectrum of **15** is found to exhibit a higher order pattern, with $\delta(^{31}\text{P})$ (ⁱPr₂P) = 6.22 ppm, $\delta(^{31}\text{P})$ (1-AdPH) = 2.45 ppm, $^1J(\text{PP}) = 245.97$ Hz.²⁸ The ¹H NMR spectrum shows a doublet at 3.92 ppm



$[^1J(\text{PH}) = 297.49$ Hz]. A $^2J(\text{PH})$ coupling constant cannot be discerned in the spectrum. The protons of both isopropyl groups in the ¹H NMR spectrum give rise to partially overlapping higher-order spin systems and while an exact assignment is impossible, the isopropyl groups appear to be non-equivalent. This finding is supported by the observation of six lines for the two isopropyl groups in the ¹³C {¹H, ³¹P} NMR spectrum. For the carbon atoms of the carbonyl groups two resonances at $\delta(^{13}\text{C}) = 217.26$ ppm, $^2J(\text{PC}) = 9.39$ Hz (*cis*-CO), and $\delta(^{13}\text{C}) = 221.23$ ppm, $^2J(\text{PC}) = 4.36$ Hz (*trans*-CO), are observed. The mass spectrum exhibits the molecular ion at m/z 476, fragment ions caused by the successive loss of carbonyl groups and the fragments $[1\text{-AdP(H)P}^i\text{Pr}_2]^+$, $[1\text{-AdP(H)P}]^+$ and $[\text{Ad}]^+$. IR bands are observed for $\nu(\text{PH})$ at 2307 cm^{-1} and in the carbonyl region at 2060, 1979 and 1937 cm^{-1} .

In order to confirm the structure and identity of **15**, and to exclude the possibility of a migration of the $\text{Cr}(\text{CO})_5$ group to the more nucleophilic diisopropyl-substituted phosphorus atom, a single-crystal X-ray diffraction study of **15** was conducted (Fig. 2, Table 3). This confirms the presence of an adamantyl-substituted and pentacarbonyl-chromium-coordinated diphosphine. The main distortion from ideal octahedral coordination geometry

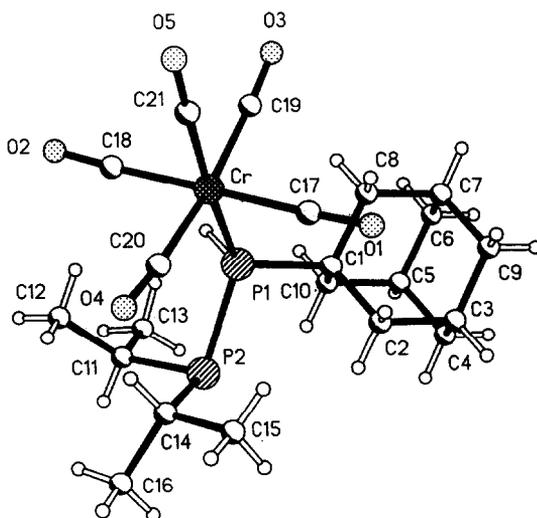


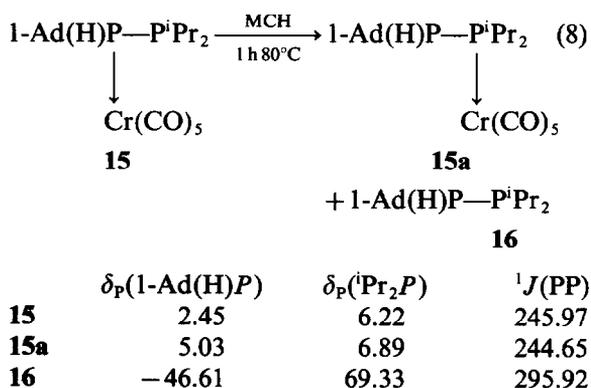
Fig. 2. X-ray crystal structure of compound **15**.

Table 3. Selected bond lengths (pm) and angles (°) for compound **15**

Cr—P(1)	245.9(1)	Cr—C(17)	190.7(2)
Cr—C(18)	189.9(2)	Cr—C(19)	189.9(2)
Cr—C(20)	190.9(2)	Cr—C(21)	185.7(2)
P(1)—P(2)	223.6(1)	P(1)—C(1)	188.4(2)
P(2)—C(11)	186.5(2)	P(2)—C(14)	185.2(2)
O(1)—C(17)	113.9(2)	O(2)—C(18)	113.8(2)
O(3)—C(19)	113.8(2)	O(4)—C(20)	113.6(3)
O(5)—C(21)	114.7(2)		
P(1)—Cr—C(17)	91.6(1)	P(1)—Cr—C(18)	89.1(1)
C(17)—Cr—C(18)	178.9(1)	P(1)—Cr—C(19)	88.5(1)
C(17)—Cr—C(19)	91.7(1)	C(18)—Cr—C(19)	89.2(1)
P(1)—Cr—C(20)	100.6(1)	C(17)—Cr—C(20)	89.6(1)
C(18)—Cr—C(20)	89.5(1)	C(19)—Cr—C(20)	170.8(1)
P(1)—Cr—C(21)	172.3(1)	C(17)—Cr—C(21)	90.0(1)
C(18)—Cr—C(21)	89.4(1)	C(19)—Cr—C(21)	83.9(1)
C(20)—Cr—C(21)	86.9(1)	Cr—P(1)—P(2)	128.3(1)
Cr—P(1)—C(1)	119.2(1)	P(2)—P(1)—C(1)	100.2(1)
P(1)—P(2)—C(11)	103.8(1)	P(1)—P(2)—C(14)	102.7(1)
C(11)—P(2)—C(14)	103.1(1)	P(1)—C(1)—C(2)	110.9(1)
P(1)—C(1)—C(8)	109.4(1)	P(1)—C(1)—C(10)	110.2(1)
P(2)—C(11)—C(12)	116.9(1)	P(2)—C(11)—C(13)	111.1(1)
C(12)—C(11)—C(13)	112.0(1)	P(2)—C(14)—C(15)	109.0(1)
P(2)—C(14)—C(16)	109.4(1)	Cr—C(17)—O(1)	177.9(1)
Cr—C(18)—O(2)	176.3(1)	Cr—C(19)—O(3)	173.4(1)
Cr—C(20)—O(4)	173.2(1)	Cr—C(21)—O(5)	177.3(2)

is indicated by the angles P(1)—Cr—C(20) [100.6(1)°] and C(19)—Cr—C(20) [170.8(1)°]. These wide angles are probably caused by the bulky isopropyl substituents at P(2), which lie approximately synclinal (skew) and synperiplanar (partially eclipsed) relative to the pentacarbonyl-chromium grouping [torsion angles: Cr—P(1)—P(2)—C(11) 93.7°; Cr—P(1)—P(2)—C(14) -13.4°]. The P(1)—P(2) bond length is normal [223.6(1) pm]. The P(1)—C(1) bond length [188.4(2) pm] is slightly greater than P—C bonds in species involving less bulky alkyl substituents, but is comparable with P—C bond lengths in other adamantyl phosphines.¹³ The adamantyl group shows, as expected, a narrow range of values for the C—C bond lengths [152.1(2) C(6)—C(7) to 154.6(3) C(5)—C(10); av. 153.2 pm]. P(1) shows a considerably distorted tetrahedral coordination geometry associated with the bulky substituents Cr(CO)₅ and P(ⁱPr)₂, which effect a widening of the angle Cr—P(1)—P(2) [128.3(1)°]. The less bulky part of the diisopropylphosphine substituent faces the adamantyl substituent and the angle P(2)—P(1)—C(1) is thus small [100.2(1)°]. The coordination geometry at P(2) is pyramidal; the average angle at P(2) is 103.2°.

Finally, a solution of **15** in methylcyclohexane was heated to 80°C. Within 1 h the resonances of compound **15** disappeared in the ³¹P NMR spectrum and a new AB spin system was observed. This was assigned to the isomeric complex **15a**, the result of the migration of the Cr(CO)₅ group to the diisopropyl-substituted phosphorus atom. The following ³¹P NMR parameters are observed for **15a**: δ(³¹P) (1-AdPH) = 5.03 ppm, δ(³¹P) (ⁱPr₂P) = 6.89 ppm, ¹J(PP) = 244.65 Hz.²⁸ Additional doublets at δ(³¹P) = -46.61 and 69.33 ppm [¹J(PP) = 295.92 Hz] are assigned to the thermally liberated free ligand 1,1-diisopropyl-2-(1-adamantyl)diphosphine **16**; the signal at lower field



arises from the $^1\text{Pr}_2\text{P}$ group, the one at higher field from the 1-AdPH group [eq. (8)]. After a 6 h heating period (80°C) ^{31}P NMR signals of **15a** and **16** are no longer observed. Instead complicated, partially overlapping patterns due to higher order spectra are seen and the signals can no longer be unambiguously assigned.

EXPERIMENTAL

All experiments were conducted in an atmosphere of dry, oxygen-free nitrogen in conventional glass apparatus.²⁹ Solvents were purified by standard procedures, dried and stored over molecular sieves.^{30,31} The following compounds were synthesized according to procedures given in the literature: 1-adamantylphosphine,³² bis-(1-adamantyl)-phosphine,³³ diiron enneacarbonyl,³⁴ triiron dodecacarbonyl,³⁵ diphenylchlorophosphine³⁶ and diisopropylchlorophosphine.³⁷

NMR spectra (CDCl_3). Bruker AC-200 (^1H at 200.1 MHz, ^{13}C at 50.3 MHz, ^{31}P at 81.0 MHz). Chemical shifts are given in ppm vs int. CDCl_3 (^1H , ^{13}C) and 85% H_3PO_4 ext. (^{31}P), coupling constants are listed in Hz. Chemical shift values were given a

positive sign when the absorption, relative to the standard, was at low field and *vice versa*. Multiplicities: s = singlet, d = doublet, m = multiplet.

IR spectra. Beckman IR 4260 and Nicolet FT-IR 740. Except for **15** (solution in chloroform), the IR spectra were recorded on hexane solutions. Absorption frequencies are quoted in wave numbers (cm^{-1}). Intensities: vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

Mass spectra. Finnigan MAT 8430. Samples were introduced into the mass spectrometer via a direct inlet septum (EI ionization).

Analyses. Microanalytical Laboratory Beller (Göttingen) and Analytical Laboratory of the Institut für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig.

Abbreviations. MCH = methylcyclohexane. THF = tetrahydrofuran.

Synthesis of the phosphine complexes 1–6 (Table 4)

General procedure. Approximately equimolar amounts of the phosphine and of the appropriate metal carbonyl were dissolved or suspended in the

Table 4. Preparation of compounds 1–6

Educts	Solvent	Yield	Analytical data
	Reaction conditions Melting point		
1 1-AdPH ₂ (1.63 g, 9.7 mmol) Cr(CO) ₆ (2.31 g, 10.5 mmol)	Diglyme (40 cm ³)	130°C/7 h 146°C 2.87 g (82.3%)	C ₁₅ H ₁₇ CrO ₅ P (360.266) Found: C, 50.07; H, 4.81; P, 8.48. Calc.: C, 50.01; H, 4.76; P, 8.60%.
	Decaline (30 cm ³)		
	100°C/10 h 121°C 2.97 g (73.5%)		
2 1-AdPH ₂ (1.68 g, 10.0 mmol) Mo(CO) ₆ (3.90 g, 14.8 mmol)	Decaline (30 cm ³)	100°C/12 h 128°C 2.59 g (52.9%)	C ₁₅ H ₁₇ MoO ₅ P (404.210) Found: C, 44.54; H, 4.41; P, 7.65. Calc.: C, 44.57; H, 4.24; P, 7.66%.
	Decaline (30 cm ³)		
	100°C/12 h 128°C 2.59 g (52.9%)		
3 1-AdPH ₂ (1.68 g, 10.0 mmol) W(CO) ₆ (5.82 g, 16.5 mmol)	Diglyme (60 cm ³)	130°C/6 h 206°C (dec.) 2.22 g (86.3%)	C ₁₅ H ₁₇ O ₅ PW (490.104) Found: C, 36.95; H, 3.43; P, 6.28. Calc.: C, 36.76; H, 3.08; P, 6.32%.
	Diglyme (60 cm ³)		
	130°C/7 h 168°C (dec.) 1.94 g (72.1%)		
4 1-Ad ₂ PH (1.57 g, 5.2 mmol) Cr(CO) ₆ (1.27 g, 5.8 mmol)	Diglyme (60 cm ³)	130°C/9 h 178°C (dec.) 1.81 g (54.4%)	C ₂₅ H ₃₁ CrO ₅ P (494.487) Found: C, 60.95; H, 6.50; P, 6.20. Calc.: C, 60.72; H, 6.32; P, 6.26%.
	Diglyme (60 cm ³)		
	130°C/7 h 168°C (dec.) 1.94 g (72.1%)		
5 1-Ad ₂ PH (1.51 g, 5.0 mmol) Mo(CO) ₆ (1.49 g, 5.6 mmol)	Diglyme (70 cm ³)	140°C/9 h 178°C (dec.) 1.81 g (54.4%)	C ₂₅ H ₃₁ MoO ₅ P (538.431) Found: C, 55.91; H, 5.90; P, 5.78. Calc.: C, 55.77; H, 5.80; P, 5.75%.
	Diglyme (70 cm ³)		
	140°C/9 h 178°C (dec.) 1.81 g (54.4%)		
6 1-Ad ₂ PH (1.60 g, 5.3 mmol) W(CO) ₆ (1.92 g, 5.5 mmol)	Diglyme (70 cm ³)	140°C/9 h 178°C (dec.) 1.81 g (54.4%)	C ₂₅ H ₃₁ O ₅ PW (626.341) Found: C, 48.60; H, 5.36; P, 5.03. Calc.: C, 47.94; H, 4.99; P, 4.95%.
	Diglyme (70 cm ³)		
	140°C/9 h 178°C (dec.) 1.81 g (54.4%)		

degassed solvent and heated until the evolution of CO ceased. Subsequently, the reaction mixtures were kept at -18°C overnight. The precipitate thus obtained was collected by filtration and was purified by recrystallization from THF.

Mass spectra. 1: 360 (10) [M]⁺, 332 (1) [M-CO]⁺, 304 (6) [M-2CO]⁺, 276 (10) [M-3CO]⁺, 248 (30) [M-4CO]⁺, 220 (100) [M-5CO]⁺, 135 (10) [Ad]⁺. 2: 406 (24) [M]⁺, 378 (20) [M-CO]⁺, 350 (60) [M-2CO]⁺, 322 (38) [M-3CO]⁺, 294 (100) [M-4CO]⁺, 266 (60) [M-5CO]⁺, 135 (85) [Ad]⁺. 3: 492 (6) [M]⁺, 464 (12) [M-CO]⁺, 436 (100) [M-2CO]⁺, 408 (14) [M-3CO]⁺, 380 (16) [M-4CO]⁺, 352 (6) [M-5CO]⁺, 15 (12) [Ad]⁺. 4: 494 (4) [M]⁺, 466 (3) [M-CO]⁺, 438 (3) [M-2CO]⁺, 410 (6) [M-3CO]⁺, 382 (20) [M-4CO]⁺, 354 (100) [M-5CO]⁺, 302 (10) [Ad₂PH]⁺, 135 (70) [Ad]⁺. 5: 540 (1) [M]⁺, 512 (2) [M-CO]⁺, 484 (5) [M-2CO]⁺, 456 (3) [M-3CO]⁺, 428 (1) [M-4CO]⁺, 400 (1) [M-5CO]⁺, 302 (18) [Ad₂PH]⁺, 135 (100) [Ad]⁺. 6: 626 (10) [M]⁺, 598 (25) [M-CO]⁺, 570 (40) [M-2CO]⁺, 542 (8) [M-3CO]⁺, 514 (6) [M-4CO]⁺, 486 (10) [M-5CO]⁺, 302 (4) [Ad₂PH]⁺, 135 (100) [Ad]⁺.

Synthesis of 7 and 8 (data for 8 in square brackets)

A mixture of Fe₂(CO)₉ (5 g, 13.7 mmol) [0.55 g, 1.5 mmol] and 2.25 g/13.3 mmol (0.45 g/1.5 mmol) of the appropriate phosphine in degassed toluene (60 cm³) [70 cm³] was stirred for 16 h [96 h] at room temperature. Subsequently, the reaction mixtures were filtered and the solvent removed *in vacuo* (0.1 mm). The crude products thus left were recrystallized from THF.

7: Yield: 3.94 g (88.1%); m.p.: 92°C (dec.). Found: C, 50.1; H, 5.4; Fe, 16.7. Calc. for C₁₄H₁₇FeO₄P (336.107): C, 50.0; H, 5.1; Fe, 16.6%. Mass spectrum: 336 (12) [M]⁺, 308 (12) [M-CO]⁺, 280 (10) [M-2CO]⁺, 252 (90) [M-3CO], 224 (100) [M-4CO]⁺, 135 (40) [Ad]⁺. 8: Yield: 0.52 g (73.7%); m.p.: 117°C . Found: C, 61.5; H, 6.7; Fe, 12.0. Calc. for C₂₄H₃₁FeO₄P (470.327): C, 61.3; H, 6.6; Fe, 11.9%. Mass spectrum: 470 (3) [M]⁺, 442 (5) [M-CO]⁺, 414 (1) [M-2CO]⁺, 386 (60) [M-3CO]⁺, 358 (40) [M-4CO]⁺, 302 (14) [Ad₂PH]⁺, 279 (10) [M-2CO-Ad]⁺, 135 (100) [Ad]⁺.

Preparation of 9, 10 and 11

A mixture of 1-AdPH₂ (5 g, 29.7 mmol) and Fe₃(CO)₁₂ (15 g, 29.8 mmol) in toluene (170 cm³) was heated at 100°C for 14 h. The reaction mixture

was allowed to cool to room temperature and was filtered through 5 g of silica gel. The solvent was removed from the filtrate at 0.1 mm. A ³¹P NMR spectrum (CDCl₃) showed signals due to 9, 10 and 11. This material was sublimed at 100°C (0.1 mm) until no more 9 was deposited on the cold finger. The residue was twice recrystallized from hexane and 11 was obtained as dark red rhombohedral crystals.

9: Yield: 3.54 g (20.3%, based on 1-AdPH₂); m.p.: 200°C (dec.). Found: C, 38.7; H, 3.1; Fe, 28.4. Calc. for C₁₉H₁₇Fe₃O₉P (587.853): C, 38.8, H, 2.9; Fe, 28.5. Mass spectrum: 588 (22) [M]⁺, 560 (12) [M-CO]⁺, 532 (16) [M-2CO]⁺, 504 (100) [M-3CO]⁺, 474 (44) [M-4CO]⁺, 446 (38) [M-5CO]⁺, 418 (90) [M-6CO]⁺, 390 (20) [M-7CO]⁺, 362 (12) [M-8CO]⁺, 334 (30) [M-9CO]⁺, 200 (36) [Fe₃PH]⁺, 199 (34) [Fe₃P]⁺, 135 (14) [Ad]⁺. 10: Yield: 7.26 g (65.0%, based on 1-AdPH₂); m.p.: $>240^{\circ}\text{C}$. Found: C, 46.9; H, 4.0; Fe, 21.8. Calc. for C₂₉H₃₀Fe₃O₉P₂ (752.039): C, 46.3; H, 4.0; Fe, 22.3%. Mass spectrum: 752 (<1) [M]⁺, 724 (5) [M-CO]⁺, 696 (12) [M-2CO]⁺, 668 (10) [M-3CO]⁺, 640 (<1) [M-4CO]⁺, 612 (14) [M-5CO]⁺, 584 (16) [M-6CO]⁺, 556 (10) [M-7CO]⁺, 528 (8) [M-8CO]⁺, 500 (24) [M-9CO]⁺, 444 (12) [Fe₂P₂Ad₂]⁺, 365 (13) [Fe₃P₂Ad]⁺, 309 (6) [Fe₂P₂Ad]⁺, 230 (11) [Fe₃P₂]⁺, 199 (5) [Fe₃P]⁺, 135 (100) [Ad]⁺.

Synthesis of 12 and 13 (data for 13 in square brackets)

A mixture of Ni(CO)₄ (2.07 g, 12 mmol) [2.55 g, 15 mmol] and 1-AdPH₂ [1.69 g, (10 mmol)] or (1-Ad)₂PH [1.51 g, 5 mmol] was stirred in THF (40 cm³) over 5 h at room temperature until the evolution of CO had ceased. Upon removal of the solvent *in vacuo* (0.1 mm) 12 was left as a colourless oil, 13 as a colourless solid.

12: Yield: 2.17 g (69.9%). Found: C, 49.8; H, 5.5; P, 10.1. Calc. for C₁₃H₁₇NiO₃P (310.949): C, 50.2; H, 5.5; P, 10.0%. Mass spectrum: 310 (1) [M]⁺, 282 (12) [M-CO]⁺, 254 (20) [M-2CO]⁺, 226 (28) [M-3CO]⁺, 168 (4) [AdPH₂]⁺, 135 (100) [Ad]⁺. 13: Yield: 1.51 g (67.8%); m.p.: $94-96^{\circ}\text{C}$. Found: C, 61.8; H, 7.4; P, 7.0. Calc. for C₂₃H₃₁NiO₃P (445.170): C, 62.1; H, 7.0; P, 7.0%. Mass spectrum: 416 (6) [M-CO]⁺, 388 (10) [M-2CO]⁺, 360 (16) [M-3CO]⁺, 302 (10) [Ad₂PH]⁺, 135 (100) [Ad]⁺.

Preparation of 11a/11b

A solution of 7 (1.35 g, 4 mmol) in toluene (70 cm³) was refluxed for 6 h. A product/educt ratio

of 1 : 1 was determined by ^{31}P NMR spectroscopy. This ratio was unchanged after a further 2 h reflux period. The reaction mixture was cooled to room temperature, filtered through 2 g of silica gel and the solvent removed *in vacuo* (0.1 mm). The reaction mixture was separated by column chromatography (10 g of silica gel; mobile phase n-pentane). The mixture of **11a/11b** was obtained as the first, bright yellow fraction. Unreacted **7** (orange-brown) was recovered as a second fraction. Subsequently, the solvent was removed from both fractions *in vacuo* (0.1 mm).

11a/11b: Yield: 0.53 g (43.1%); m.p.: 140°C (dec). Found: C, 50.9; H, 5.4; Fe, 18.2. Calc. for $\text{C}_{26}\text{H}_{32}\text{Fe}_2\text{O}_6\text{P}_2$ (614.177): C, 50.8; H, 5.2; Fe, 18.2%. ^1H NMR: δ 1.67–2.07 [m, 1-Ad], 2.82–5.15 [m, P—H]. IR spectrum: $\nu = 2052$ (m), 2015 (vs), 1983 (s), 1973 (s). Mass spectrum: 614 (16) $[\text{M}]^+$, 586 (14) $[\text{M}-\text{CO}]^+$, 558 (40) $[\text{M}-2\text{CO}]^+$, 530 (50) $[\text{M}-3\text{CO}]^+$, 502 (12) $[\text{M}-4\text{CO}]^+$, 474 (4) $[\text{M}-5\text{CO}]^+$, 446 (60) $[\text{M}-6\text{CO}]^+$, 394 (18) $[\text{M}-3\text{CO}-\text{AdH}]^+$, 366 (22) $[\text{M}-4\text{CO}-\text{AdH}]^+$, 338 (23) $[\text{M}-5\text{CO}-\text{AdH}]^+$, 310 (22) $[\text{M}-6\text{CO}-\text{AdH}]^+$, 174 (100) $[\text{Fe}_2\text{P}_2]^+$, 135 (24) $[\text{Ad}]^+$.

Attempted reaction of **7** with $\text{Fe}_3(\text{CO})_{12}$

A mixture of **7** (1.8 g, 5.7 mmol) and $\text{Fe}_3(\text{CO})_{12}$ (2.52 g, 5 mmol) in toluene (60 cm^3) was heated, first at 80°C for 12 h, then refluxed for a further 3 h. At both stages only the signal of unchanged **7** was observed in the ^{31}P NMR spectrum.

Attempted reaction of **2** with $\text{Ph}_2\text{PCl}/\text{NEt}_3$

A mixture of **2** (1.01 g, 2.5 mmol), Ph_2PCl (1.20 g, 5.4 mmol) and NEt_3 (1.1 g, 11 mmol) in toluene (60 cm^3) was stirred, first at room temperature for 7 days, then heated at reflux for a further 5 h. No precipitation of $[\text{HNEt}_3]\text{Cl}$ was observed, nor was there a change in the ^{31}P NMR spectrum.

Preparation of **15**

To a suspension of **1** (0.75 g, 2.1 mmol) in a mixture of 10 cm^3 each of diethyl ether and toluene, held at -196°C , was added a 15% solution of $^n\text{BuLi}$ (0.9 g, 2.1 mmol) in hexane *ca* 6 g of a 15% solution via a syringe. The temperature of the reaction mixture was allowed to increase to -78°C . During 0.5 h of stirring the reaction mixture turned orange, accompanied by evolution of a gaseous product (^nBuH). Subsequently, $^1\text{Pr}_2\text{PCl}$ (0.4 g, 2.6 mmol) in toluene (5 cm^3) was added dropwise over 5 min. The mixture was warmed to room tem-

perature, stirred for 2 h and filtered to remove the LiCl . The solvent was removed from the filtrate *in vacuo* (0.1 mm) and the remaining yellow product recrystallized from hexane, giving crystals suitable for the X-ray crystal structure determination.

15: Yield: 0.77 g (77%); m.p.: 121–124°C. Found: C, 53.0; H, 6.4; P, 12.8. Calc. for $\text{C}_{21}\text{H}_{30}\text{CrO}_5\text{P}_2$ (476.41): C, 52.9; H, 6.3; P, 13.0%. NMR spectra: ^1H : δ 1.10–1.29 [m, $-\text{CH}_3$], 1.71–2.10 [m, 1-Ad], 2.12–2.32 [m, $-\text{CH}(\text{CH}_3)_2$], 3.92 [d, PH, $^1J(\text{PH}) = 297.49$]. $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$: δ 20.19, 23.25 [s, $-\text{CH}(\text{CH}_3)_2$], 20.40, 21.09, 22.41, 24.28 [s, $-\text{CH}(\text{CH}_3)_2$], 29.11 [s, C^3 (1-Ad)], 35.94 [s, C^1 (1-Ad)], 36.17 [s, C^4 (1-Ad)], 41.89 [s, C^2 (1-Ad)], 217.29 [s, CO_{cis}], 221.20 [s, CO_{trans}]. $^{13}\text{C}\{^1\text{H}\}$: δ 19.89–24.51 [m, $\{\text{CH}_3\}_2\text{CH}-$], 28.98–35.88 [m, C^1 (1-Ad), C^3 (1-Ad)], 36.14 [s, C^4 (1-Ad)], 41.83 [d, C^2 (1-Ad)], $^2J(\text{PC}) = 7.09$, 217.26 [d, CO_{cis}], $^2J(\text{PC}) = 9.39$, 221.23 [d, CO_{trans}], $^2J(\text{PC}) = 4.36$. IR spectrum: $\nu = 2307$ (w), 2060 (s), 1979 (m), 1937 (vs). Mass spectrum: 476 (3) $[\text{M}]^+$, 448 (19) $[\text{M}-\text{CO}]^+$, 364 (32) $[\text{M}-4\text{CO}]^+$, 336 (100) $[\text{M}-5\text{CO}]^+$, 284 (9) $[\text{M}-5\text{CO}-\text{Cr}]^+$, 242 (6) $[\text{M}-5\text{CO}-\text{Cr}-\text{C}_3\text{H}_6]^+$, 200 (52) $[\text{M}-5\text{CO}-\text{Cr}-2\text{C}_3\text{H}_6]^+$, 135 (31) $[\text{Ad}]^+$.

X-ray crystal structure determination of 15: Crystal data: $\text{C}_{21}\text{H}_{30}\text{CrO}_5\text{P}_2$. $M = 476.4$, triclinic, space group $\text{P}\bar{1}$, $a = 1019.2(3)$, $b = 1077.7(3)$, $c = 1125.7(3)$ pm, $\alpha = 84.10(3)$, $\beta = 74.61(3)$, $\gamma = 78.10(3)$, $U = 1.165 \text{ nm}^3$, $Z = 2$, $D_x = 1.358 \text{ mg m}^{-3}$. $\lambda(\text{Mo}-K_\alpha) = 0.71069 \text{ \AA}$, $\mu = 0.66 \text{ mm}^{-1}$, $T = 173 \text{ K}$, $F(000) = 500$.

Data collection and reduction. A cut yellow prism $1.0 \times 0.65 \times 0.50 \text{ mm}$ was mounted on a glass fibre and transferred to the cold gas stream of the diffractometer (Siemens R3 with LT-2 low-temperature attachment). Data were collected to $2\theta_{\text{max}} 55^\circ$. Cell constants were refined from setting angles of 50 reflections in the range $2\theta 20\text{--}23^\circ$. An absorption correction based on ψ -scans was applied (transmission factors: 0.62–0.66). Of 9018 reflections 5374 were unique ($R_{\text{int}} = 0.025$) and $4727 > 4\sigma(F)$ were used for all calculations (Program system “Siemens SHELXTL PLUS”).

Structure solution and refinement. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. The hydrogen bonded to phosphorus was then the second largest peak in a difference Fourier synthesis and was kept fixed at the peak position during the final cycles. Refinement proceeded to $R = 0.030$, $wR = 0.041$. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0002F^2$. 262 parameters; $S = 1.8$; max, $\Delta/\sigma = 0.003$; max, $\Delta\rho = 0.8 \times 10^{-6} \text{ e pm}^{-3}$. Full details of the structure determination have

been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD 57330.

Thermolysis of 15, formation of 15a and 16

A solution of 15 (50 mg, 0.1 mmol) in MCH (6 cm³) was heated at 80°C for 6 h. ³¹P NMR spectra of the reaction mixture were recorded at the beginning of the heating period, after 1 h and after 6 h. The experiment was terminated after 6 h because signals from unknown decomposition products were observed.

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