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Synthesis and characterisation of 2,6-diisopropylphenylimido complexes of chromium in oxidation states IV–VI

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The chromium(VI) imido complex $Cr(NAr)_2Cl_2$ (Ar = 2,6-$^iPr_2C_6H_3$) reacted with pyridine and PMe_3 to form the monoadducts $Cr(NAr)_2Cl_2(py)$ **1** and $Cr(NAr)_2Cl_2(PMe_3)$ **2** respectively. The reaction between $Cr(NAr)_2Cl_2$ and LiNHAr afforded the amide complex $Cr(NAr)_2(NHAr)Cl$ **3**. Attempts to generate the half-sandwich species $CrCp(NAr)_2Cl$ through treatment of the dichloride with LiCp, $Mg(Cp)_2$ or NaCp resulted in the dimeric chromium(V) complex $[Cr(NAr)(\mu\text{-}NAr)Cl]_2$ **4**. Reduction of $Cr(NAr)_2Cl_2$ with magnesium in the presence of PMe_3 or PMe_2Ph afforded the chromium(IV) bis-phosphine complexes $Cr(NAr)_2(PMe_3)_2$ **5** and $Cr(NAr)_2(PMe_2Ph)_2$ **6** respectively. The reaction between $Cr(NAr)_2(PMe_3)_2$ and phenyldiazomethane gave the diazoalkane complex $Cr(NAr)_2(N_2CHPh)(PMe_3)$ **7**. Complexes **1**, **3**, **4** and **7** have been structurally characterised.

Introduction

The bis(imido) chemistry of chromium has, until recently, been restricted to the *tert*-butylimido ligand first accessed by Nugent and Harlow[1a] through the reaction of CrO_2Cl_2 with four equivalents of the silylated amine $(Me_3Si)NH^tBu$. More recently, we have exploited a related procedure to synthesize adamantylimido derivatives of the type $Cr(NAd)_2X_2$ (X = siloxide, halide or alkyl)[2] and have also developed a general access point to 2,6-diisopropylphenylimido derivatives *via* aniline exchange reactions with *tert*-butylimido precursors.[3] In parallel studies, Wilkinson and co-workers[4] reported the synthesis of the related 2,6-dimethylphenylimido species *via* treatment of *tert*-butylimido precursors with aryl isocyanates. A particular advantage of the adamantylimido and arylimido derivatives over their *tert*-butylimido counterparts is their enhanced crystallinity;[2,5] this is most notable for the dialkyl species, where the adamantylimido and arylimido compounds are isolable as crystalline materials whereas the *t*-butylimido derivatives exist as oils. The chemistry of the arylimido systems has briefly been explored by ourselves,[3,5] and Wilkinson and co-workers.[4,6] Here, we report full details of the synthesis and characterisation of a further series of chromium species containing 2,6-diisopropylphenylimido ligands.

Results and discussion

Adduct formation

The reaction between $Cr(NAr)_2Cl_2$ and an excess of pyridine in pentane precipitates the monoadduct $Cr(NAr)_2Cl_2(py)$ **1** as a purple microcrystalline solid in good (79%) yield (Scheme 1). In an NMR scale reaction between $Cr(NAr)_2Cl_2$ and PMe_3 (1 equivalent) the monophosphine adduct $Cr(NAr)_2Cl_2(PMe_3)$ **2** was generated in quantitative yield (by ^1H NMR spectroscopy). Attempts to isolate **2** were unsuccessful, with rapid decomposition to paramagnetic side products being observed. No reaction is observed between $Cr(NAr)_2Cl_2$ and the bulkier phosphine PPh_3 (60 °C, 3 d) in contrast to the *tert*-butylimido analogue which cleanly forms $Cr(N^tBu)_2Cl_2(PPh_3)$.[7]

The ^1H and ^{13}C NMR spectra of compounds **1** and **2** each show a single set of resonances corresponding to the imido ligands, consistent with a five-co-ordinate species that is rapidly equilibrating between trigonal bipyramidal and square-based pyramidal geometries in solution (Berry rotation). In order to establish the thermodynamically preferred geometry at the chromium centre in these adducts, a crystal structural analysis

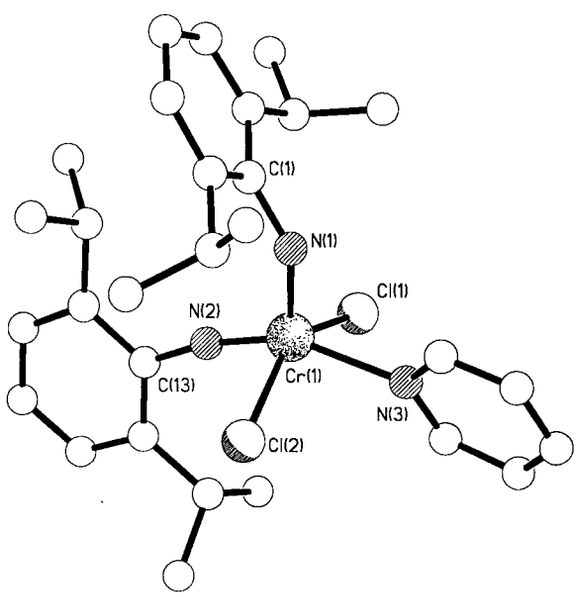
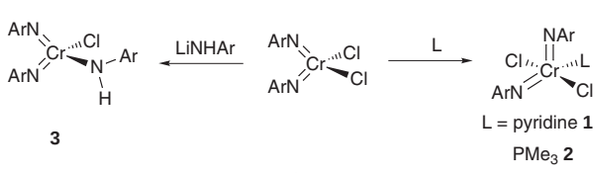


Fig. 1 The molecular structure of compound **1A**.



Scheme 1 The syntheses of $Cr(NAr)_2Cl_2(py)$ **1**, $Cr(NAr)_2Cl_2(PMe_3)$ **2** and $Cr(NAr)_2(NHAr)Cl$ **3**.

Table 1 Selected bond lengths (Å) and angles (°) for the monoclinic (A) and triclinic (B) structures of $Cr(NAr)_2Cl_2(py)$ **1**, with estimated standard deviations (e.s.d.s) in parentheses

	A	B
Cr(1)–N(1)	1.673(2)	1.679(2)
Cr(1)–N(2)	1.671(3)	1.660(2)
Cr(1)–N(3)	2.135(2)	2.159(2)
Cr(1)–Cl(1)	2.2994(10)	2.2893(7)
Cr(1)–Cl(2)	2.3042(10)	2.3035(7)
N(1)–C(1)	1.391(4)	1.384(3)
N(2)–C(13)	1.354(4)	1.356(3)
N(1)–Cr(1)–N(2)	110.99(12)	109.36(9)
N(1)–Cr(1)–N(3)	98.86(11)	96.10(8)
N(1)–Cr(1)–Cl(1)	103.13(9)	107.81(7)
N(1)–Cr(1)–Cl(2)	106.04(9)	106.94(7)
N(2)–Cr(1)–Cl(1)	88.89(9)	90.50(6)
Cl(1)–Cr(1)–N(3)	81.50(7)	83.51(6)
N(3)–Cr(1)–Cl(2)	81.64(7)	81.20(6)
Cl(2)–Cr(1)–N(2)	92.42(9)	89.16(6)
N(2)–Cr(1)–N(3)	150.03(11)	154.44(8)
Cl(1)–Cr(1)–Cl(2)	148.15(4)	143.22(3)
Cr(1)–N(1)–C(1)	148.9(2)	147.8(2)
Cr(1)–N(2)–C(13)	172.6(2)	169.1(2)

was performed on complex **1**. Suitable crystals were grown from saturated CH_2Cl_2 or toluene at −30 °C.† Fig. 1 shows the structure of **1**; important bond lengths and angles are collected in Table 1.

The geometry around chromium is best described as distorted square pyramidal, although it can also be described as a distorted trigonal bipyramid. In the former case the two chlorides, one imido and the pyridine form the base of the structure, with the other imido ligand in the apical position. The angles around the base of the structure range from 81 to 93°, with the chloride ligands *trans* to one another, and the chromium atom located 0.56 Å out of the basal plane of the pyramid. The pyridine and phenyl ring of the basal aryl(imido) rings are both approximately perpendicular to the basal plane (71 and 83° respectively), presumably to minimise steric interactions with the chloride ligands.

The $Cr–N_{imido}$ distances [Cr(1)–N(1) 1.673(2); Cr(1)–N(2) 1.671(3) Å] are relatively long compared to those of four-co-ordinate $Cr(NAr)_2X_2$ complexes [1.642(2)–1.660(4) Å],[3,8] a consequence of the increased electron density at the metal centre causing a reduction in the $Cr–N_{imido}$ bond order. An analogous increase is observed in $Cr(N^tBu)_2Cl_2$ [Cr–N 1.623 Å average] when 1 equivalent of PMe_2Ph is co-ordinated [$Cr(N^tBu)_2Cl_2(PMe_2Ph)$: Cr–N 1.640 Å average].[1d,4]

The two angles at the imido nitrogen atoms differ significantly from one another, with the value for the basal ligand in the range normally associated with 'linear' imido ligands [Cr(1)–N(2)–C(13) 172.6(2)°] and the apical imido group exhibiting notable distortion [Cr(1)–N(1)–C(1) 148.9(2)°].[9a] Concomitant with this 'bending' is an increase in the $N–C_{ipso}$ bond length [N(1)–C(1) 1.391(4), *cf.* N(2)–C(13) 1.354(4) Å] indicative of a reduced bond order between the nitrogen and phenyl rings, and a localisation of electron density at the nitrogen atom. This 'bending' effect can be rationalised by considering a trigonal bipyramidal geometry around chromium. In this case the pyridine and the 'linear' imido group occupy the two axial positions while the two chlorides and the 'bent' imido take up the equatorial positions. When viewed as such the structure is then comparable to the compound $Mo(NAr)_2Me_2(PMe_3)$, Ar = 2,6-$^iPr_2C_6H_3$, which also has a 'bent' equatorial imido group in a distorted trigonal bipyramidal structure.[9b] In fact, similar situations have been observed for other trigonal bipyramidal bis(imido)molybdenum compounds, where the bending has been attributed to electronic effects rather than crystal packing.[9a]

† Compound **1** crystallises in the monoclinic crystal system (space group $P2_1/c$) when isolated from CH_2Cl_2 (**1A**) and in the triclinic crystal system (space group $P\bar{1}$) when isolated from toluene (**1B**). In both cases a square pyramidal arrangement of ligands about the chromium is found, with only slight differences in bond lengths/angles. The best fit of the atoms comprising the two co-ordination spheres has a rms deviation of 0.082 Å. The principal differences are small changes in the relative orientations of the aromatic rings. The structure of **1A** is described in the text.

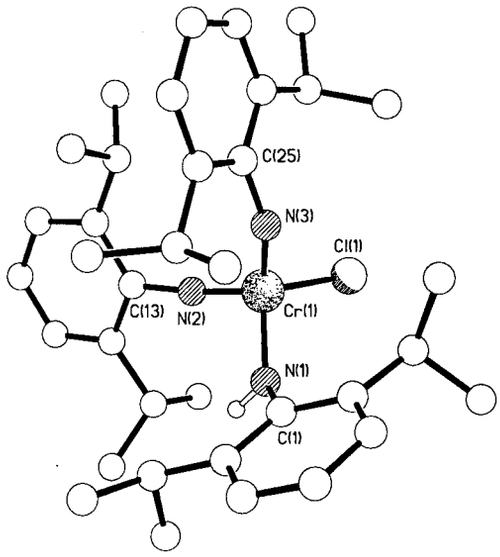


Fig. 2 The molecular structure of compound **3**.

Attempted synthesis of the $[Cr(NR)_3]$ functionality

Initial work by Wilkinson and co-workers[1c,d] on the *tert*-butylimido complexes of chromium failed to access the tris-imido complex $Cr(N^tBu)_3$. Interaction of the arylimido complex $Cr(Nmes)_2Cl_2$ (mes = 2,4,6-$Me_3C_6H_2$) with LiNHmes afforded $[Li(Et_2O)_2][Cr(Nmes)_3(NHmes)]$, which resisted further deprotonation.[6b]

Our initial attempts at synthesizing $Cr(NAr)_3$ derivatives employed $Cr(NAr)_2(NH^tBu)Cl$ as a starting material.[3] Heating a sample to 60 °C does not eliminate HCl, even in the presence of a base such as NEt_3. Attempts to deprotonate the amide ligand with ^{t}BuLi were also unsuccessful, resulting in recovery of the starting material. An attempt to synthesize a mixed bis-amide product *via* treatment of $Cr(NAr)_2(NH^tBu)Cl$ with LiNHAr (with a view to inducing a subsequent proton transfer and liberation of Bu^tNH_2) also gave starting material.

Reaction of the dichloride $Cr(NAr)_2Cl_2$ with LiNHAr proceeds smoothly in THF to afford $Cr(NAr)_2(NHAr)Cl$ **3** in 60% yield (Scheme 1). The ^{1}H NMR spectrum reveals a low field signal (δ 12.22) assigned to the amide proton, with the corresponding N–H stretch appearing at 3345 cm^{-1} in the infrared spectrum. The highly fluxional nature of the molecule is evident from ^{1}H and ^{13}C NMR spectroscopy. At room temperature a single methine resonance is observed integrating to four protons, assigned to the imido ligand substituents. The remaining methine resonance of the amide aryl group is broadened into the baseline, and the corresponding isopropyl methyl signal (δ 1.23) is also broadened. Two sets of aryl resonances are however clearly evident in a 2:1 ratio. The ^{1}H NMR data collected at −20 °C reveal three separate methine resonances, corresponding to the amide ligand and two inequivalent imido groups, suggesting that at this temperature rotation about the $Cr–N_{amide}$ bond is slow on the NMR timescale.

Crystals of compound **3** suitable for an X-ray study were isolated from a concentrated pentane solution cooled to −30 °C. Fig. 2 shows the molecular structure; important bond lengths and angles are collected in Table 2. The co-ordination at

Table 2 Selected bond lengths (Å) and angles (°) for $Cr(NAr)_2(NHAr)Cl$ **3**, with e.s.d.s in parentheses

Cr(1)–N(1)	1.843(3)	Cr(1)–N(2)	1.651(3)
Cr(1)–N(3)	1.657(3)	Cr(1)–Cl(1)	2.2297(10)
N(1)–C(1)	1.418(4)	N(2)–C(13)	1.386(4)
N(3)–C(25)	1.388(4)		
		N(1)–Cr(1)–N(3)	108.73(12)
N(1)–Cr(1)–N(2)	105.34(13)	N(1)–Cr(1)–Cl(1)	112.94(10)
N(2)–Cr(1)–N(3)	114.69(13)	N(3)–Cr(1)–Cl(1)	109.37(9)
N(2)–Cr(1)–Cl(1)	105.80(10)	Cr(1)–N(2)–C(13)	172.7(2)
Cr(1)–N(1)–C(1)	135.6(2)		
Cr(1)–N(3)–C(25)	157.3(2)		

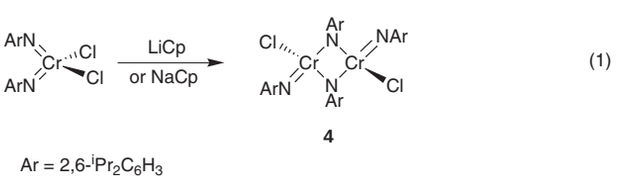
chromium is distorted tetrahedral with interligand angles in the range 105–115°; the largest angle predictably is located between the multiply bonded imido ligands. The $Cr–N_{imido}$ bond lengths [Cr(1)–N(2) 1.651(3), Cr(1)–N(3) 1.657(3) Å] are comparable to those found in other arylimidochromium complexes.[3,8] The $Cr–N_{amide}$ bond length [Cr(1)–N(1) 1.843(3) Å] is slightly longer than in $Cr(NAr)_2(NH^tBu)Cl$ [1.813(3) Å],[3] a consequence of π bonding between the amide nitrogen atom and the *ipso*-carbon of the aryl ring reducing the $Cr–N_{amide}$ bonding order.

The Cr(1)–N(2)–C(13) angle of 172.7(2)° is typical of a 'linear' imido ligand, whilst the Cr(1)–N(3)–C(25) angle is more noticeably bent at 157.3(2)°. The substituents of the amide ligand, rather than lying within the sterically more accommodating N(1)–Cr(1)–Cl(1) plane, are directed towards the imido groups, a consequence of the competition for available metal π-symmetry orbitals.[10] Attempts to convert **3** into $Cr(NAr)_3$ were unsuccessful.

Attempted synthesis of cyclopentadienyl derivatives

The synthesis of the cyclopentadienyl complex $CrCp(N^tBu)_2Cl$ has been reported from the reaction of $Cr(N^tBu)_2Cl_2$ with $MgCp_2(THF)_{2.5}$ ($Cp = \eta\text{-}C_5H_5$).[1b] The complex is isolated as purple crystals in low (33%) yield, but is unstable in C_6D_6 (16 h, 25 °C). Wilkinson and co-workers[6] have been successful in isolating and structurally characterising a range of pentamethylcyclopentadienyl mesitylimido complexes of chromium. We were interested in determining whether the bulk of the 2,6-$^iPr_2C_6H_3$ substituent of the imido group would be sufficient to stabilise unsubstituted Cp derivatives, $CrCp(NAr)_2X$.

The attempted reaction of $Cr(NAr)_2Cl_2$ with $(Me_3Si)Cp$ (60 °C, THF, 16 h) afforded only starting material on work-up. The reaction with LiCp (in THF), $Mg(Cp)_2$ (in THF) or NaCp (in Et_2O), however, afforded a purple-red crystalline solid, **4**, eqn. (1). Crystals of **4** suitable for an X-ray study were grown



(1)

4

Ar = 2,6-$^iPr_2C_6H_3$

from a concentrated pentane solution cooled to −30 °C. Fig. 3 illustrates the molecular structure; bond lengths and angles are collected in Table 3. The structure of **4** contains two independent dimeric molecules in the asymmetric unit, each metal centre bearing one terminal and one bridging imido group, and a terminal chloride. An analogous complex has been isolated from the reaction of ArN=C=O with $Cr(N^tBu)_2Cl_2$, where terminal arylimido groups and bridging *tert*-butylimido groups are observed.[4] The bridge in **4** is essentially symmetrical, with Cr–N distances of 1.84 Å (average). The distances to the terminal imido groups are unremarkable [average 1.65 Å] and the chromium–chlorine bond lengths [average 2.206 Å] are consistent with a high oxidation state metal centre. The Cr_2N_2 ring is

Table 3 Selected bond lengths (Å) and angles (°) for the two independent molecules (A and B) of $[Cr(NAr)(\mu\text{-}NAr)Cl]_2$ **4** with e.s.d.s in parentheses

	A	B
Cr(1)–N(1)	1.640(7)	1.646(6)
Cr(1)–N(2)	1.865(8)	1.836(7)
Cr(1)–N(4)	1.823(7)	1.819(7)
Cr(1)–Cl(1)	2.207(2)	2.204(3)
Cr(2)–N(2)	1.859(7)	1.837(7)
Cr(2)–N(3)	1.654(7)	1.648(6)
Cr(2)–N(4)	1.830(7)	1.831(6)
Cr(2)–Cl(2)	2.211(2)	2.202(2)
Cr(1)···Cr(2)	2.476(2)	2.474(2)
N(1)–C(5)	1.382(11)	1.386(10)
N(2)–C(17)	1.414(11)	1.419(11)
N(3)–C(29)	1.380(10)	1.391(10)
N(4)–C(41)	1.419(11)	1.415(10)
N(1)–Cr(1)–N(4)	112.2(3)	112.0(3)
N(1)–Cr(1)–N(2)	112.3(3)	111.5(3)
N(4)–Cr(1)–N(2)	95.6(3)	95.2(3)
N(1)–Cr(1)–Cl(1)	110.4(2)	109.6(2)
N(4)–Cr(1)–Cl(1)	103.0(2)	103.6(2)
N(2)–Cr(1)–Cl(1)	121.7(2)	123.4(2)
N(3)–Cr(2)–N(4)	110.9(3)	111.0(3)
N(3)–Cr(2)–N(2)	111.0(3)	112.0(3)
N(4)–Cr(2)–N(2)	95.6(3)	94.8(3)
N(3)–Cr(2)–Cl(2)	111.5(2)	110.8(2)
N(4)–Cr(2)–Cl(2)	104.9(2)	102.9(2)
N(2)–Cr(2)–Cl(2)	121.3(2)	123.3(2)
C(5)–N(1)–Cr(1)	176.3(6)	174.9(6)
C(17)–N(2)–Cr(2)	137.2(6)	137.2(5)
C(17)–N(2)–Cr(1)	138.5(5)	138.0(5)
Cr(2)–N(2)–Cr(1)	83.4(3)	84.7(3)
C(29)–N(3)–Cr(2)	171.0(6)	172.8(6)
C(41)–N(4)–Cr(1)	136.2(6)	139.9(5)
C(41)–N(4)–Cr(2)	138.4(5)	134.7(5)
Cr(1)–N(4)–Cr(2)	85.4(3)	85.4(3)

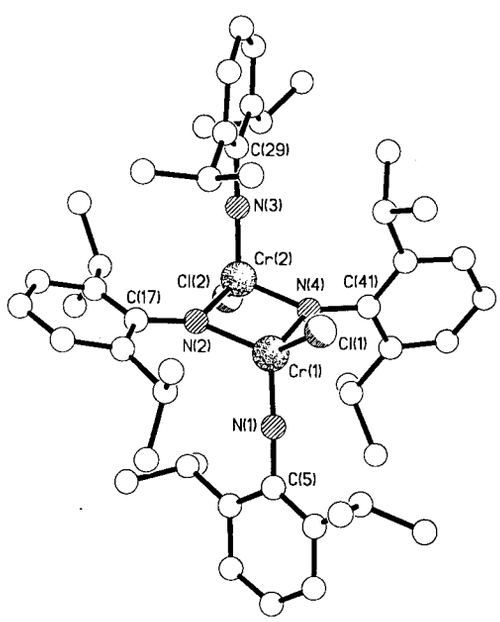


Fig. 3 The molecular structure of compound **4**.

planar to within 0.004 Å. The internal angles at the chromium atoms are larger than those found at the nitrogen atoms (N–Cr–N 95.3 average; Cr–N–Cr 84.7° average), consistent with some metal–metal interaction. The Cr···Cr distance of 2.476(2) Å is comparable to that reported in the related complex $[Cr(NAr)(\mu\text{-}N^tBu)Cl]_2$ (Cr···Cr 2.475(2) Å average).

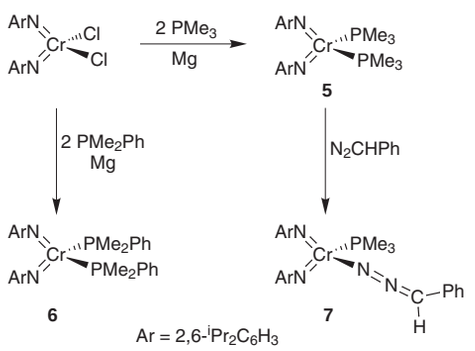
Although complex **4** contains two chromium(V) centres, it is diamagnetic, believed to be due to spin coupling *via* the bridging imido ligands or *via* the Cr···Cr interaction. The room temperature ^1H NMR spectrum gives a singlet resonance

assignable to eight equivalent isopropyl methine hydrogens. The spectrum does not change upon cooling to −30 °C, implying that the terminal and bridging imido ligands are exchanging rapidly on the NMR timescale.

Synthesis of chromium(IV) bis-phosphine complexes

Bis-phosphine complexes of Group 4 bent metallocenes and Group 5 half sandwich imido complexes have been reported and shown to react with unsaturated substrates.[11,12] Recently, this area of chemistry has been extended to include the bis(imido) complexes of molybdenum.[13] Attempts to synthesize the analogous chromium species $Cr(N^tBu)_2(PMe_3)_2$ through the reduction of $Cr(N^tBu)_2Cl_2$ with magnesium in the presence of PMe_3 afforded a small amount of paramagnetic material which could not be fully characterised.[7]

The reaction between $Cr(NAr)_2Cl_2$ and magnesium was performed in the presence of 2.1 equivalents PMe_3, to afford $Cr(NAr)_2(PMe_3)_2$ **5** in 46% yield (Scheme 2). The compound is



Scheme 2 The syntheses of $Cr(NAr)_2(PMe_3)_2$ **5**, $Cr(NAr)_2(PMe_2Ph)_2$ **6** and $Cr(NAr)_2(N_2CHPh)(PMe_3)$ **7**.

isolated as very air sensitive green crystals from a saturated pentane solution cooled to −30 °C. In an analogous reaction, $Cr(NAr)_2(PMe_2Ph)_2$ **6** was synthesized in 40% yield. The ^1H NMR spectra of both complexes are consistent with C_{2v} symmetric structures. Although crystals of sufficient quality for an X-ray study were not forthcoming, it is anticipated that these d^2 bis(imido) complexes will adopt a tetrahedral geometry,[14] as observed in $W(NAr)_2(PMe_2Ph)_2$.[15]

Attempted synthesis of a chromium alkylidene complex

We have recently reported the synthesis and isolation of the first stable chromium(IV) alkylidene complexes, by trapping the product of alkane elimination from $Cr(NAr)_2(CH_2CMe_3)_2$.[16] Although fully characterised, structural information on the alkylidene products has thus far proved elusive. In an effort to obtain a benzylidene derivative, which is not accessible *via* elimination of toluene from $Cr(NAr)_2(CH_2Ph)_2$, we treated $Cr(NAr)_2(PMe_3)_2$ with phenyldiazomethane. Such an approach has been used in the generation of well defined ruthenium metathesis catalysts $RuCl_2(=CHR')(PR_3)_2$ developed by Grubbs and co-workers,[17] and a related reaction between $VCp(NAr)(PMe_3)_2$ and $Ph_3P{=}CHPh$ afforded a vanadium(v) benzylidene complex.[18]

The reaction between $Cr(NAr)_2(PMe_3)_2$ and phenyldiazomethane gave, on work-up, purple-red crystals of the unexpected chromium diazoalkane product $Cr(NAr)_2(N_2CHPh)(PMe_3)$ **7** (Scheme 2). This can also be more conveniently synthesized in a "one-pot" reaction starting from the reduction of compound **1** with magnesium in the presence of PMe_3. This avoided the isolation of crystals of $Cr(NAr)_2(PMe_3)_2$, which is difficult to accomplish in high yield. The overall yield of the "one-pot" reaction based on the starting amount of **1** was also comparable to that of the reaction using $Cr(NAr)_2(PMe_3)_2$ as the starting material.

The ^1H NMR spectrum did not show the presence of a low field singlet associated with the highly deshielded alkylidene proton, but revealed a singlet at δ 6.46 assigned to N_2CHPh. Elemental analysis was consistent with this formula, although repeated attempts at mass spectrometry (EI, CI and FAB^+) revealed only the presence of ligand ions, presumably due to the instability of the compound.

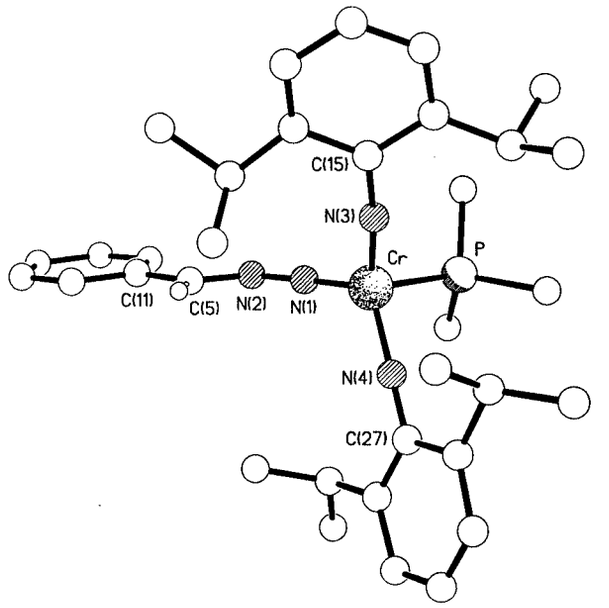


Fig. 4 The molecular structure of compound **7**.

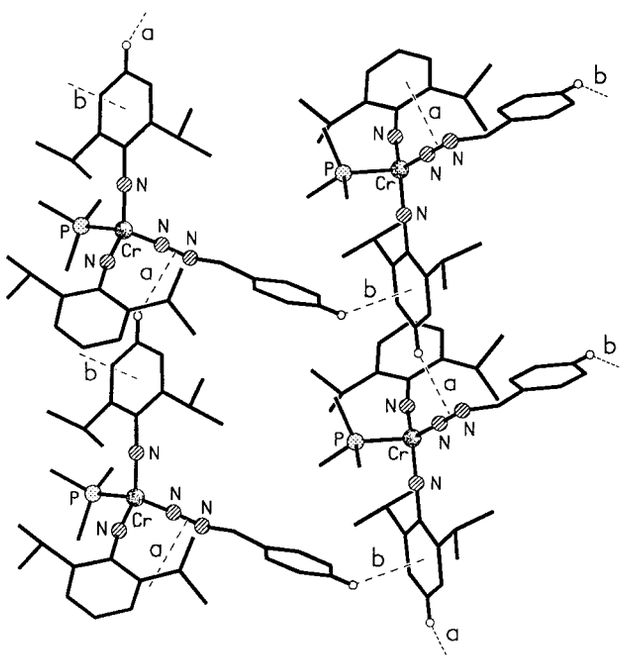


Fig. 5 Part of one of the extended C–H · · · π linked corrugated sheets of molecules in crystals of compound **7**. H · · · π distances (Å) and C–H · · · π angles (°): **a**, 2.72, 142; **b**, 2.82, 140.

In order to establish the precise structure of compound **7** an X-ray study was performed on crystals isolated from a concentrated pentane solution cooled to −30 °C. Fig. 4 shows the molecular structure; selected bond lengths and angles are collected in Table 4. The geometry at chromium is distorted tetrahedral tending towards trigonal pyramidal with the three nitrogen atoms forming the basal plane and the phosphorus the apex; the chromium lies 0.33 Å out of the 'basal' plane. The smallest angles are P–Cr–N(1) and P–Cr–N(4), being 99.0(1) and 96.9(1)° respectively. The imido ligands are linear with angles at nitrogen of 171.9(3) [N(3)] and 178.1(2)° [N(4)] and Cr–N distances of 1.675(3) and 1.671(3) Å respectively.

Table 4 Selected bond lengths (Å) and angles (°) for $Cr(NAr)_2(N_2CHPh)(PMe_3)$ **7** with e.s.d.s in parentheses

Cr–N(1)	1.716(3)	Cr–N(3)	1.675(3)
Cr–N(4)	1.671(3)	Cr–P	2.3206(11)
N(1)–N(2)	1.239(4)	N(2)–C(5)	1.323(5)
N(3)–C(15)	1.388(4)	N(4)–C(27)	1.368(4)
N(4)–Cr–N(3)	121.72(14)	N(4)–Cr–N(1)	113.9(2)
N(3)–Cr–N(1)	113.4(2)	N(4)–Cr–P	96.93(10)
N(3)–Cr–P	107.27(10)	N(1)–Cr–P	98.98(13)
N(2)–N(1)–Cr	171.8(3)	N(1)–N(2)–C(5)	123.8(4)
C(15)–N(3)–Cr	171.9(3)	C(27)–N(4)–Cr	178.1(2)
N(2)–C(5)–C(11)	120.0(4)		

The diazoalkane ligand [N(1)–N(2) 1.239(4), Cr–N(1) 1.716(3) Å] binds to the chromium centre in a singly bent co-ordination mode. The Cr–N(1)–N(2) and N(1)–N(2)–C(5) angles [171.8(3) and 123.8(4)° respectively] fall within the range normally associated with such a co-ordination mode, although no prior structurally characterised examples of chromium(VI) diazoalkane compounds are known.[19] The molecules are loosely linked *via* pairs of C–H · · · π interactions; the *para* proton of the N(4) imido group is directed towards the N=N bond of the diazoalkane ligand (a in Fig. 5) and the *para* proton of the phenyl group on the diazoalkane ligand is directed into the aryl ring of the N(4) imido group (b in Fig. 5). These interactions combine to produce extended corrugated sheets of molecules.

Complex **7** does not readily eliminate nitrogen to afford the desired alkylidene complex. Heating an NMR sample of it in C_6D_6 to 50 °C did not give rise to the expected low field signal for an alkylidene proton, but rather to a number of new signals accompanied by a broadening of the existing signals, attributed to decomposition.

In conclusion, the chromium imido complex $Cr(NAr)_2Cl_2$ forms monoadduct species with pyridine and PMe_3. Its reaction with LiNHAr generates the bis(imido) amide complex $Cr(NAr)_2(NHAr)Cl$, which could not be converted into $Cr(NAr)_3$. Attempted generation of the cyclopentadienyl derivatives resulted in isolation of the chromium(V) dimer $[Cr(NAr)(\mu\text{-}NAr)Cl]_2$. The dichloride can be reduced to the chromium(IV) complexes $Cr(NAr)_2(PMe_2R)_2$ (R = Me or Ph) by treatment with magnesium in the presence of phosphine. The attempted generation of an alkylidene species by treatment of $Cr(NAr)_2(PMe_3)_2$ with phenyldiazomethane gave the diazoalkane complex $Cr(NAr)_2(N_2CHPh)(PMe_3)$ which was found to be stable to N_2 elimination.

Experimental

General

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Departments of Chemistry at Durham and Imperial College. The NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400.0 (^{1}H), 100.6 (^{13}C) and 161.9 MHz (^{31}P) and, where stated, on a Bruker AM-500 spectrometer at 500.0 (^{1}H) and 125.8 MHz (^{13}C) and on a AM-250 spectrometer at 250.0 (^{1}H), 62.9 (^{13}C) and 101.3 MHz (^{31}P); chemical shifts are referenced to the residual protio impurity of the deuteriated solvent. The IR spectra (Nujol mulls, CsI or NaCl windows) were obtained on Perkin-Elmer 1600 FTIR and 577 grating spectrophotometers, mass spectra on a VG 7070E instrument [70 eV, 100 μA emission]. The following chemicals were prepared by previously published procedures or modifications thereof: PMe_3,[20] $Cr(NAr)_2Cl_2$,[3] N_2CHPh,[21] $Mg(Cp)_2$;[22] LiNHAr was prepared by treatment of $ArNH_2$ with ^{n}BuLi. All other chemicals were obtained commercially and used as received unless stated otherwise: pyridine (distilled under N_2); PMe_2Ph (distilled and stored over molecular sieves); NEt_3 (distilled under N_2).

Preparations

$Cr(NAr)_2Cl_2(py)$ 1. Pyridine (0.08 cm^3, 1.06 mmol) was added to a solution of $Cr(NAr)_2Cl_2$ (0.25 g, 0.53 mmol) in pentane (30 cm^3) at room temperature, resulting in formation of a purple precipitate. The suspension was stirred for 16 h. Removal of the volatiles *in vacuo* afforded $Cr(NAr)_2Cl_2(py)$ as a purple microcrystalline solid. Analytically pure samples were obtained by recrystallisation of a concentrated CH_2Cl_2 solution at −78 °C. Yield 0.23 g, 79%. Calc. for $C_{29}H_{39}Cl_2CrN_3$: C, 63.0; H, 7.1; N, 7.6. Found: C, 63.2; H, 7.1; N, 7.7%. IR: 1603w, 1577m, 1461vs (br), 1260m, 1215m, 1173w, 1154w, 1093m (br), 1073m, 1015m, 932w, 799s, 760s, 723s, 692s, 637m and 533w cm^{-1}. (EI$^+$ MS: *m/z*, (^{35}Cl) 472, [M − py]$^+$. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.97 (br s, 2 H, pyridine H_{ortho}), 7.89 (br t, 1 H, pyridine H_{para}), 7.50 (br t, 2 H, pyridine H_{meta}), 7.19–7.12 (m, 6 H, C_6H_3), 3.73 (sept, J_{HH} = 6.8 Hz, 4 H, C*H*Me$_2$) and 1.12 (d, J_{HH} = 6.8 Hz, 24 H, CH*Me*$_2$). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 162.1 (s, C_6H_3 C_{ipso}), 149.5 (d, J_{CH} = 182, pyridine C_{ortho}), 149.2 (s, C_6H_3 C_{ortho}), 138.0 (d, J_{CH} = 166, pyridine C_{para}), 132.1 (d, J_{CH} = 161, C_6H_3 C_{para}), 124.7 (d, J_{CH} = 166, pyridine C_{meta}), 122.8 (d, J_{CH} = 159, C_6H_3 C_{meta}), 29.1 (d, J_{CH} = 130, *C*HMe$_2$) and 23.91 (q, J_{CH} = 127 Hz, CH*Me*$_2$).

$Cr(NAr)_2Cl_2(PMe_3)$ 2. Trimethylphosphine (0.04 mmol) was added *via* a gas bulb to a frozen (−196 K) solution of $Cr(NAr)_2Cl_2$ (0.02 g, 0.04 mmol) in C_6D_6 (0.8 cm^3). No visible change occurred on warming to room temperature. The ^{1}H NMR spectrum however was consistent with the formation of $Cr(NAr)_2Cl_2(PMe_3)$ (100% NMR yield). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 6.95–6.85 (m, 6 H, C_6H_3), 4.03 (sept, J_{HH} = 6.6, 4 H, C*H*Me$_2$), 1.53 (d, J_{PH} = 10.8, 9 H, PMe_3), 1.12 (d, J_{HH} = 6.4 Hz, 24 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6, 100.6 MHz, 298 K): δ 161.4 (s, C_6H_3 C_{ipso}), 148.2 (s, C_6H_3 C_{ortho}), 131.6 (d, J_{CH} = 161, C_6H_3 C_{para}), 123.0 (d, J_{CH} = 158, C_6H_3 C_{meta}), 29.2 (d, J_{CH} = 131, *C*HMe$_2$), 24.2 (q, J_{CH} = 126 Hz, CH*Me*$_2$) and 14.15 (d, J_{PC} = 21 Hz, PMe_3). ^{31}P NMR (C_6D_6, 162 MHz, 298 K): δ 8.12 (s, PMe_3).

$Cr(NAr)_2(NHAr)Cl$ 3. A solution of $Cr(NAr)_2Cl_2$ (1.00 g, 2.12 mmol) in THF (50 cm^3) was cooled to −78 °C and added to LiNHAr (0.39 g, 2.12 mmol) in THF (20 cm^3) at −78 °C. The mixture was slowly allowed to attain room temperature and stirred for 18 h. The volatiles were removed *in vacuo* and the product was extracted from LiCl with pentane. Concentration and cooling of the pentane solution to −30 °C afforded pure $Cr(NAr)_2(NHAr)Cl$ as purple crystals. Yield (3 crops) 0.78 g (60%). Calc. for $C_{36}H_{52}ClCrN_3$: C, 70.4; H, 8.5; N, 6.8. Found: C, 70.0; H, 9.1; N, 6.5%. IR: 3345m, 1581w, 1262m (br), 1224w, 1177m, 1095m (br), 983w, 933m, 801s, 759vs, 753vs, 663w, 618m, 589w, 428m, 252s and 236vs cm^{-1}. (EI$^+$ MS, *m/z* (^{35}Cl) 614, [M]$^+$; 438, [M − NAr]$^+$. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 12.22 (br s, 1H, N*H*Ar), 7.03 (m, 3 H, NHAr C_6H_3), 6.85 (m, 6 H, NAr C_6H_3), 4.00 (sept, J_{HH} = 6.8 Hz, 4 H, C*H*Me$_2$), 1.23 (d, J_{HH} = 6.8, 12 H, CH*Me*$_2$ (amide)) and 1.06 (d, J_{HH} = 6.8 Hz, 24 H, CH*Me*$_2$ (imide)). ^{13}C NMR (C_6D_6, 100.6 MHz, 298 K): δ 160.8 (s, C_6H_3 C_{ipso}), 153.8 (s, C_6H_3 C_{ipso}), 146.6 (s, C_6H_3 C_{ortho}), 141.2 (s, C_6H_3 C_{ortho}), 129.2 (d*, C_6H_3 C_{para}), 123.7 (d, J_{CH} = 157, C_6H_3 C_{meta}), 122.93 (d, J_{CH} = 158, C_6H_3 C_{meta}), 29.0 (d, J_{CH} = 129, *C*HMe$_2$) and 28.9 (q*, CH*Me*$_2$). ^{13}C NMR ($C_6D_5CD_3$, 101 MHz, 193 K): δ 160.9, 160.5, 146.5, 146.2, 25.6, 24.8, 23.7 and 22.9 (* splitting obscured by solvent peak or other signals).

$[Cr(NAr)(\mu\text{-}NAr)Cl]_2$ 4. *Procedure A.* A solution of LiCp (0.03 g, 0.44 mmol) in THF (20 cm^3) was cooled to −78 °C and

Table 5 Crystallographic data for compounds **1A**, **1B**, **3**, **4** and **7**

	1A	**1B**	**3**	**4**	**7**
Formula	$C_{29}H_{39}Cl_2CrN_3$	$C_{29}H_{39}Cl_2CrN_3$	$C_{36}H_{52}ClCrN_3$	$C_{48}H_{68}Cl_2Cr_2N_4$	$C_{34}H_{49}CrN_4P$
M	552.5	552.5	614.3	876.0	596.7
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	10.465(3)	9.5275(8)	10.4714(11)	12.483(2)	9.9487(7)
b/Å	8.896(2)	10.7197(10)	15.411(2)	19.584(3)	18.5847(7)
c/Å	31.961(8)	15.5038(14)	21.493(2)	40.908(5)	18.7972(7)
α/°		97.572(2)			
β/°	98.45(3)	105.819(5)	94.707(2)	92.598(10)	90.884(4)
γ/°		104.820(2)			
U/Å^3	2943.2(13)	1437.8(2)	3456.7(6)	9991(2)	3475.1(3)
Z	4	2	4	8	4
D_c/g cm^{-3}	1.247	1.276	1.180	1.165	1.141
μ/mm^{-1}	0.59	0.61	0.44	0.58	3.33
T/K	160	160	160	293	203
$R_1(F^2 > 2\sigma)$	0.0438	0.0447	0.0588	0.0697	0.0535
$wR_2(F^2$, all data)	0.1152	0.1184	0.1248	0.1792	0.1469
Data, parameters	5163, 324	6189, 325	5729, 386	12850, 1009	5141, 350

added to a solution of $Cr(NAr)_2Cl_2$ (0.20 g, 0.42 mmol) in THF (20 cm^3) at −78 °C. The reaction was allowed to warm to room temperature and stirred for 12 h. Removal of the volatiles *in vacuo* afforded a red, oily solid. The product was extracted from LiCl with heptane and cooled to −30 °C, affording dark purple crystals. Yield (3 crops) 0.18 g, 96% (based on amount of starting Cr).

Procedure B. The compound $Cr(NAr)_2Cl_2$ (0.27 g, 0.56 mmol) and NaCp (0.05 g, 0.60 mmol) were mixed as solids in a dry-box. Diethyl ether (30 cm^3) was cooled to 0 °C and added to the mixture. After stirring for 12 h at room temperature the solvent was removed *in vacuo* and the product was extracted with pentane. Concentration and cooling to −30 °C afforded $[Cr(NAr)(\mu\text{-}NAr)Cl]_2$. Yield (3 crops) 0.23 g, 92%.

Procedure C. The compound $Cr(NAr)_2Cl_2$ (0.30 g, 0.63 mmol) and $Mg(Cp)_2$ (0.05 g, 0.32 mmol) were mixed as solids in a dry-box and cooled to −78 °C. Cold THF (−78 °C) was then added and stirred at −78 °C for 10 min before being allowed to warm to room temperature and left to stir for 16 h. The solvent was then removed. Extraction into pentane (50 cm^3) and cooling to −30 °C gave crystals of $[Cr(NAr)(\mu\text{-}NAr)Cl]_2$. Yield 0.06 g, 22%. Calc. for $C_{24}H_{34}ClCrN_2$: C, 65.8; H, 7.8; N, 6.4. Found: C, 65.7; H, 7.6; N, 6.2%. IR: 2727m, 2352w, 1581m, 1263s, 1155m, 805s, 722s and 408m. (FAB$^+$ MS: m/z (^{35}Cl) 437, [0.5 M − H]$^+$. ^{1}H NMR (C_6D_6, 250 MHz, 298 K): δ 6.84–6.71 (m, 12 H, C_6H_3), 3.95 (sept, J_{HH} = 6.8, 8 H, C*H*Me$_2$), 1.20 (d, J_{HH} = 6.8, 24 H, CH*Me*$_2$) and 1.13 (d, J_{HH} = 6.8 Hz, 24 H, CH*Me*$_2$). ^{13}C NMR ($CDCl_3$, 62.9 MHz, 298 K): δ 162.6 (s, C_6H_3 C_{ipso}), 147.1 (s, C_6H_3 C_{ortho}), 130.3 (d, J_{CH} = 160, C_6H_3 C_{meta}), 122.6 (d, J_{CH} = 160, C_6H_3 C_{para}), 28.9 (d, J_{CH} = 131, *C*HMe$_2$) and 23.6 (q, J_{CH} = 126 Hz, CH*Me*$_2$).

$Cr(NAr)_2(PMe_3)_2$ 5. Trimethylphosphine (0.22 cm^3, 2.11 mmol) was condensed onto a solution of $Cr(NAr)_2Cl_2$ (0.25 g, 0.53 mmol) and activated magnesium turnings (0.014 g, 0.58 mmol) in THF (50 cm^3) cooled to −196 °C. The solution was stirred for 0.5 h at −78 °C. The reaction mixture was allowed to warm to room temperature and 1 atm of nitrogen introduced. The volatiles were removed by vacuum after 16 h. The product was extracted with pentane and recrystallised at −30 °C to afford dark green crystals. Yield 0.14 g (46%). Calc. for $C_{30}H_{52}CrN_2P_2$: C, 65.0; H, 9.45; N, 5.05. Found: C, 65.0; H, 9.1; N, 4.9%. IR: 1918w, 1583w, 1559w, 1417m, 1357w, 1325s, 1275s, 1156w, 1100m (br), 1057w, 980s, 938vs (br), 841m, 800s, 724s, 714m, 664s, 474w (br) and 440w (br) cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.16–7.10 (m, 6 H, C_6H_3), 4.23 (sept, J_{HH} = 6.8, 4 H, C*H*Me$_2$), 1.27 (d, J_{HH} = 6.8, 24 H, CH*Me*$_2$) and 1.09 (d, J_{PH} = 6.8 Hz, 18 H, PMe_3). ^{13}C NMR (C_6D_6, 100.6 MHz, 298 K): δ 159.6 (s, C_6H_3 C_{ipso}), 142.5 (s, C_6H_3 C_{ortho}), 122.7 (d, J_{CH} = 154, C_6H_3 C_{meta}), 122.1 (d, J_{CH} = 159, C_6H_3 C_{para}), 27.9 (d, J_{CH} = 128, *C*HMe$_2$), 24.0 (q, J_{CH} = 125, CH*Me*$_2$) and 21.4 (m‡, J_{PC} = 21 Hz, P*Me*$_3$). ^{31}P NMR (C_6D_6, 162 MHz, 298 K): δ 53.71 (s, PMe_3) (m‡ denotes the X part of an ABX splitting pattern).

$Cr(NAr)_2(PMe_2Ph)_2$ 6. A mixture of $Cr(NAr)_2Cl_2$ (0.40 g, 0.85 mmol) and activated magnesium turnings (0.023 g, 0.93 mmol) in THF (50 cm^3) was cooled to −78 °C and a THF solution of PMe_2Ph (0.24 cm^3, 1.69 mmol) at −78 °C was added *via* cannula. The reaction mixture was stirred for 24 h at room temperature. The volatiles were removed *in vacuo* and the product was extracted from $MgCl_2$ as a pentane solution. Concentration and cooling to −30 °C afforded $Cr(NAr)_2(PMe_2Ph)_2$ as green crystals. Yield 0.23 g (40%). Calc. for $C_{40}H_{56}CrN_2P_2$: C, 70.8; H, 8.3; N, 4.1. Found: C, 70.5; H, 8.2; N, 3.7%. IR: 1582m, 1415s, 1355m, 1273s, 1223s, 1174w, 1156w, 1096s, 1058m, 1044m, 981s, 938s, 895s (br), 829m, 796s, 753s, 741vs, 696s, 674s, 603w (br), 560w, 489s and 421vs. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.55–6.97 (br m, 16H, C_6H_3 + PMe_2*Ph*), 4.23 (br sept, 4 H, J_{HH} = 6.8, C*H*Me$_2$), 1.35 (d, J_{PH} = 6.0, 12 H, P*Me*$_2$Ph) and 1.15 (d, J_{HH} = 6.4 Hz, 24 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6, 100.6 MHz, 298 K): δ 158.9 (s, C_6H_3 C_{ipso}), 142.5 (s, C_6H_3 C_{ortho}), 140.2 (d, J_{PC} = 33, PMe_2Ph C_{ipso}), 130.7 (m, J_{PC} = 6, PMe_2Ph C_{ortho}), 128.7 (d*, C_6H_3 C_{para}), 122.4 (d, J_{CH} = 159, C_6H_3 C_{meta}), 122.1 (d, J_{CH} = 154, PMe_2Ph C_{para}), 27.5 (d, J_{CH} = 120, *C*HMe$_2$), 23.5 (d, J_{CH} = 125 Hz, CH*Me*$_2$) and 19.7 (m‡, $^1J_{PC}$ = 22 Hz, P*Me*$_2$Ph). ^{31}P NMR (C_6D_6, 162 MHz, 298 K): δ 68.09 (s, PMe_2Ph) (* splitting obscured by overlap with solvent peak; m‡ denotes the X part of an ABX splitting pattern).

$Cr(NAr)_2(N_2CHPh)(PMe_3)$ 7. *Procedure A.* Phenyldiazomethane (2 equivalents) was added to a solution of $Cr(NAr)_2(PMe_3)_2$ (0.19 g, 0.34 mmol) in light petroleum (bp 40–60 °C, 30 cm^3) at room temperature. The reaction mixture was stirred for 30 min, after which the solvent was removed *in vacuo*. Extraction into pentane and cooling to −30 °C afforded $Cr(NAr)_2(N_2CHPh)(PMe_3)$ as purple-red crystals. Yield 0.08 g, 39%.

Procedure B: "One-pot" synthesis. A reaction between $Cr(NAr)_2Cl_2(py)$ **1** (0.25 g, 0.45 mmol), magnesium (17 mg, 1.5 equivalents) and PMe_3 (2 equivalents) was carried out in a method similar to the preparation of compound **5**. However, after 16 h, the solution was filtered off and 2 equivalents of freshly prepared phenyldiazomethane were added to the filtrate at room temperature in a method similar to procedure A above. Alternatively, the addition of phenyldiazomethane can be carried out at −78 °C, giving the same product. Yield 0.08 g, 29% from **1**. Calc. for $C_{34}H_{49}CrN_4P$: C, 68.4; H, 8.3; N, 9.4. Found:

C, 68.7; H, 8.5; N, 9.2%. IR: 2724m, 1594m, 1533w, 1324m, 1280m, 1243w, 1164w, 947m, 749m, 725m and 693w cm^{-1}. ^1H NMR (C_6D_6, 250 MHz, 298 K): δ 7.7–6.9 (m, 11 H, C_6H_3 + C_6H_5), 6.46 (s, 1 H, C*H*Ph), 4.11 (sept, J_{HH} = 6.9, 4 H, C*H*Me_2), 1.27 (d, J_{HH} = 7.0, 12 H, CH*Me*$_2$), 1.24 (d, J_{HH} = 6.9, 12 H, CH*Me*$_2$) and 1.10 (d, J_{PH} = 10.4 Hz, 9 H, PMe_3). ^{13}C NMR (C_6D_6, 125.8 MHz, 298 K): δ 159.3, 142.3, 137.3, 129.6, 129.1, 127.4, 126.7, 125.7, 125.1, 124.1, 123.2, 121.7, 105.5 (d, J_{CH} = 171, N_2*C*HPh), 28.4 (d, J_{CH} = 128, *C*HMe_2), 23.8 (q, J_{CH} = 126, CH*Me*$_2$) and 15.5 (dq, J_{PC} = 20, J_{CH} = 130 Hz, PMe_3). ^{31}P NMR (C_6D_6, 101.3 MHz, 298 K): δ 22.91 (s, PMe_3).

X-Ray crystallography

A summary of the crystal data, data collection and structure refinement parameters for compounds **1A**, **1B**, **3**, **4** and **7** is given in Table 5. A crystal of **1A** (monoclinic form of **1**) was examined on a Stoe-Siemens four-circle diffractometer, crystals of **1B** (triclinic form of **1**) and **3** on a Bruker AXS SMART CCD diffractometer, and crystals of **4** and **7** on a Siemens P4 four-circle diffractometer; Cu-Kα radiation (λ = 1.54178 Å) was used for **7**, Mo-Kα radiation (λ = 0.71073 Å) for the others. Data were corrected semiempirically for absorption. The structures were solved by automatic direct methods, and were refined on F^2 values for all unique reflections. All final difference map features were within ±0.8 e $Å^{-3}$. Programs were standard manufacturers' control software, together with SHELXTL[23] and local programs.

CCDC reference number 186/1490.

See http://www.rsc.org/suppdata/dt/1999/2633/ for crystallographic files in .cif format.

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