

TETRACARBONYL(CARBENE-PHOSPHINE) AND TETRACARBONYL(IMIDATE-PHOSPHINE) COMPLEXES OF CHROMIUM(0)

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Summary

Treatment of the carbene complexes $[(\text{CO})_5\text{Cr}\{\text{C}(\text{OEt})\text{CH}_2\text{PPh}_2\}]$ (I) with LiBu followed by alkylation with $[\text{Et}_3\text{O}][\text{BF}_4]$ gives the carbene-phosphine chelates $[(\text{CO})_4\text{Cr}\{\text{C}(\text{OEt})\text{C}(\text{OEt})(\text{Bu})\text{CH}_2\text{PPh}_2\}]$ (IV) and $[(\text{CO})_4\text{Cr}\{\text{C}(\text{OEt})\text{C}(\text{OEt})=\text{CHPPh}_2\}]$ (V). The tungsten analogs cannot be prepared similarly. With the substituted hydrazine, MeNHNH_2 at -80°C , NH addition to the carbene carbon atoms in the precursor complexes and concomitant ligand rearrangement produces the pentacarbonylphosphine compounds $[(\text{CO})_5\text{M}\{\text{PPh}_2\text{CH}_2\text{C}(\text{OEt})=\text{NH}\}]$ (VIII, IX; M = Cr, W). The heterometallocyclic carbene-phosphine compounds react by formal NH insertion into the metal–carbene bond to give the six-membered chelates $[(\text{CO})_4\text{Cr}\{\text{NH}=\text{C}(\text{OEt})\text{C}(\text{OEt})(\text{Bu})\text{CH}_2\text{PPh}_2\}]$ (X) and $[(\text{CO})_4\text{Cr}\{\text{NH}=\text{C}(\text{OEt})\text{C}(\text{OEt})=\text{CHPPh}_2\}]$ (XI). The complex $[(\text{CO})_4\text{Cr}\{\text{C}(\text{NH}_2)\text{C}(\text{OEt})=\text{CHPPh}_2\}]$ (VI), obtained by aminolysis of $[(\text{CO})_4\text{Cr}\{\text{C}(\text{OEt})\text{C}(\text{OEt})=\text{CHPPh}_2\}]$ (V), has been the subject of a single crystal X-ray diffraction study. It crystallizes in the monoclinic space group $P2_1/c$ with a 12.55(1), b 13.50(1), c 12.83(1) Å, β 90.2(1)°, V 2174 Å³ and $D(\text{calcd})$ 1.37 g cm⁻³ for mol.wt. 447.37 and $Z = 4$. The structure was refined to $R = 0.067$ and $R_w = 0.050$. The Cr–C(carbene) bond length is 2.067(5) Å and the Cr–P distance 2.352(1) Å.

Introduction

The metal carbonyl complexes $[(\text{CO})_6\text{Cr}]$ and $[(\text{CO})_6\text{W}]$ react with $\text{LiCH}(\text{SR}^1)\text{R}^2$ ($\text{R}^1 = \text{alkyl, aryl}$; $\text{R}^2 = \text{Ph, SPh}$; $\text{R}^1\text{R}^2 = (\text{CH}_2)_3\text{S}$) to produce, upon subsequent alkylation with $[\text{Et}_3\text{O}][\text{BF}_4]$ and via formal CO insertion, the carbene thioether chelates $[(\text{CO})_4\text{M}\{\text{C}(\text{OEt})\text{C}(\text{OEt})=\text{C}(\text{SR}^1)\text{R}^2\}]$ (M = Cr, W) [1]. When $\text{LiCH}(\text{PPh}_2)_2$ was used under similar conditions the corresponding reaction did not occur. A carbene-phosphine chelate has been described by Abicht and Issleib [2], but their synthesis does not involve carbonyl insertion into a metal–carbene bond.

We have shown previously [3] that treatment of the complex $[(\text{CO})_4\text{Cr}(\text{CNPh})\{\text{C}(\text{OEt})\text{CHS}(\text{CH}_2)_3\text{S}\}]$ with ammonia gives, by isocyanide insertion into the

metal-carbene bond, proton migration, and sulphur coordination, the chelate $[(\text{CO})_4\text{Cr}\{\text{C}(\text{NHPh})\text{C}(\text{OEt})=\text{CS}(\text{CH}_2)_3\text{S}\}]$. This observation prompted us to prepare neutral phosphorus-containing carbene complexes to serve as precursors for the preparation of carbene-phosphine chelates by deprotonation and via carbonyl insertion.

It is known that five-membered carbene-thioether chelates react differently from the carbenes $[(\text{CO})_5\text{M}\{\text{C}(\text{OMe})\text{Me}\}]$ ($\text{M} = \text{Cr}$ or W) with substituted hydrazines. The latter class of complexes is converted into acetonitrile complexes, $[(\text{CO})_5\text{M}(\text{NCMe})]$, with $\text{R}^1\text{R}^2\text{NNH}_2$ ($\text{R}^1 = \text{R}^2 = \text{Me}$; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Ph}$) [4], whereas the chelates undergo formal NH and/or NMe insertion upon treatment with hydrazines ($\text{R}^1 = \text{R}^2 = \text{Me}$; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$) [3]. To ascertain whether the unusual imidate moiety can also be obtained with carbene-phosphine chelates and whether NH insertion is also possible with pentacarbonyl carbene complexes (which contain a phosphine unit and could, therefore, also rearrange), we studied the reactions of all the new compounds with MeNHNH_2 .

Since complexes containing a carbene-phosphine bidentate ligand are rare, we undertook a single crystal X-ray diffraction study of such a compound, and the results are also presented here.

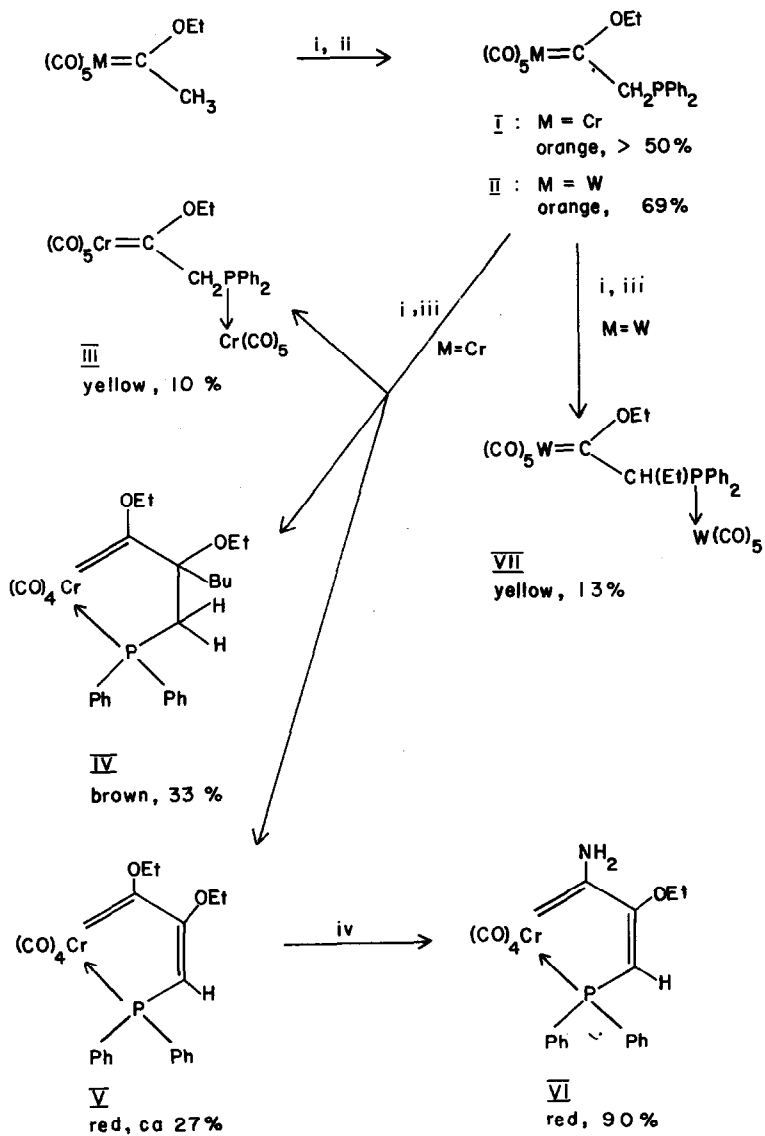
Results and discussion

Preparation of the precursor complexes I and II

Treatment of the carbene anions $[(\text{CO})_5\text{M}\{\text{C}(\text{OEt})\text{CH}_2\}]^-$ ($\text{M} = \text{Cr}$ or W) [5] with ClPPh_2 in THF gave the phosphorus-containing carbene complexes I and II (Scheme 1). Unless products I and II were separated from the reaction mixture immediately after addition of ClPPh_2 at low temperature, the yields were substantially lower. Complex I was obtained as an orange oil and was unstable. Crystals of II showed no decomposition under nitrogen. It was soluble in organic solvents such as methylene chloride, ether and hexane. Both compounds gave molecular ions in the mass spectrometer, and exhibited infrared absorption bands in the $\nu(\text{CO})$ frequency region similar to those from the parent ethoxy(methyl)carbene complexes (Table 1). The signals from the P-CH₂ protons in I appeared as a doublet ($J(\text{PCH}) > 0.5$ Hz), whereas II gave only a singlet, at δ 4.17 ppm (Table 2).

Attempts to prepare heterometallic carbene-phosphine complexes

We have shown previously that both of the moieties **1** and **2** ($\text{M} = \text{Cr}$ or W) undergo carbonylation and cyclization on deprotonation [1,3]. Both compounds I and II contain a moiety similar to **2** ($\text{M} = \text{Cr}$ or W ; $\text{X} = \text{O}$) but with the sulphur atom and its attached groups replaced by PPh_2 . On deprotonation with an equimolar amount of LiBu and subsequent alkylation, the desired product was obtained only with chromium as central metal. All the other products are also shown in Scheme 1. The products III, IV and VII were obtained analytically pure by column chromatography followed by crystallization. Compound V was isolated as an unstable oil and then converted into stable red crystals of the aminocarbene complex VI to allow complete characterization by elemental analysis. Compounds III–VII are soluble in organic solvents such as methylene chloride, ether and benzene, but less so in hexane. The oils or solutions of the crystals decompose even under nitrogen at -20°C . The crystals decompose very slowly in air but are stable under nitrogen.



SCHEME 1. Reagents: (i) LiBu (small excess); (ii) ClPPh_2 ; (iii) $[\text{Et}_3\text{O}][\text{BF}_4]$; (iv) NH_3 .

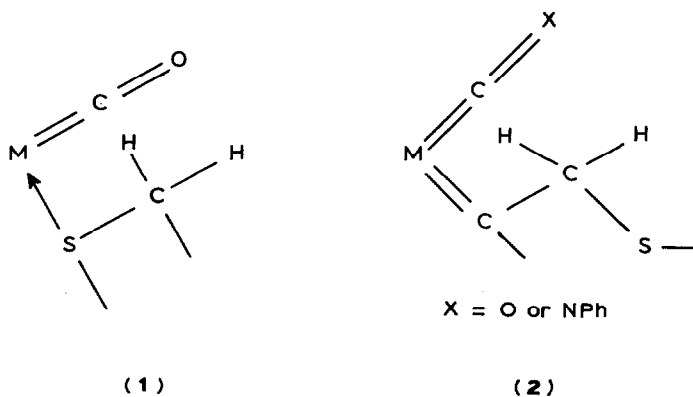


TABLE 1

INFRARED DATA ^a ($\nu(\text{CO})$ (cm^{-1}); in hexane)

	Pentacarbonyl complexes			
	$A_1^{(1)}$	B	E	$A_1^{(2)}$
I	2065m	1980w	1955(sh)	1945s
II	2075m	1979w	1951s	1941(sh)
(CO) ₅ Cr{C(OEt)Me} ^b	2064m	1979w	1947s	1961(sh)
III	2065m	1985w	1925s	1940(sh)
VII	2075m		1946s	1943(sh)
VIII	2065w		1945s	1941s
IX	2075w		1939s	1921m
A ^c	2076m	1986w	1936vs	1909m
B ^c	2075m	1944w	1979vs	1909m
	Tetracarbonyl complexes ^d			
	$A_1^{(1)}$	$A_1^{(2)}$	B ₁	B ₂
IV	2019m	1940s	1915s	1889s
V	2019m	1940s	1926s	1895m
VI	2018m	1940m	1914s	1875m
X	2018	1961s	1894s	1855m
XI	2017	1938m	1909s	1880m
C ^c	2038m	1954m	1905s	1861m

^a m, medium; s, strong; sh, shoulder; vs, very strong; w, weak. ^b Ref. 15. ^c Ref. 3. ^d Assignments based on pseudo-C_{2v} symmetry and phases of symmetry as defined by Braterman [6].

All the new compounds III–VI gave m/z values in the mass spectrometer corresponding with the respective molecular ions. For VII the ion $[M - \text{W}(\text{CO})_5]^+$ was observed. Fragmentation involved the initial loss of five (in the pentacarbonyl complex III) or four (in the tetracarbonyl complexes IV, V and VI) CO ligands. Four or three (the B₁ frequency was absent for VII) infrared absorption bands were found for the pentacarbonyl complexes in the $\nu(\text{CO})$ region. The three tetracarbonyl compounds also showed the expected four vibrations (Table 1). The four vibrations for compound V compare with the frequencies at 2032s, 1948s, 1934vs and 1886s cm^{-1} previously obtained for the carbene-thioether chelate $[(\text{CO})_4\text{Cr}\{\text{C}(\text{OEt})\text{C}(\text{OEt})=\text{C}(\text{SPh})\text{Ph}\}]$ [1].

The signals in the ¹H NMR spectra of compounds III–VI are in accord with the given structures and were assigned as in Table 2. The chemical shifts corresponding to the protons α to the phosphorus atoms deserve attention. The pentacarbonyl complex III gave a doublet for these CH₂ protons at δ 4.84 ppm owing to coupling with the ³¹P isotope ($J(\text{PCH})$ 4.5 Hz), while the corresponding resonance for the CH proton in VII appeared as a multiplet at δ 4.9 ppm. The saturated chelate ring in IV contains a chiral carbon atom. The two sp^3 protons are not equivalent, and the coupling with phosphorus gave rise to two doublets at 2.40 and 3.10 ppm. The coupling constants, $J(\text{PCH})$, were 8 and 10 Hz, respectively. The signals from the sp^2 protons α to the phosphorus atoms in compounds V and VI were found upfield, as a singlet at δ 6.30 and a doublet at 6.37 ppm, respectively.

The formation of the pentacarbonyl complexes III and VII involved replacement of a carbene ligand by a phosphorus donor atom of another similar ligand. We assumed that this low temperature substitution is due to the negative charge next to

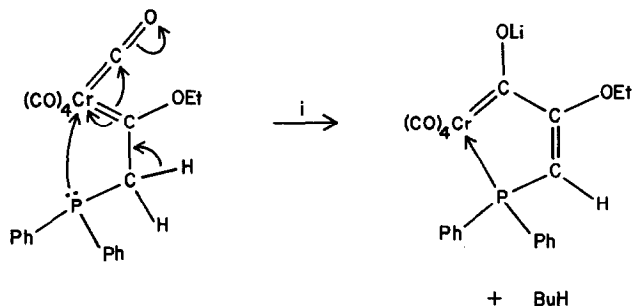
TABLE 2

¹H NMR CHEMICAL SHIFTS ^a (CDCl₃; δ rel. to int. SiMe₄)

[(CO) ₅ Cr{C(OEt)CH ₂ PPh ₂ }] ^b (I)	1.15 (t, 3H, OCH ₂ CH ₃), 4.13 (d, 2H, CH ₂), 6.37 (q, 2H, OCH ₂), 7.2 (m, 10H, Ph)
[(CO) ₅ W{C(OEt)CH ₂ PPh ₂ }] (II)	1.10 (t, 3H, OCH ₂ CH ₃), 4.17 (d, 2H, CH ₂), 4.58 (q, 2H, OCH ₂), 7.4 (m, 10H, Ph)
[(CO) ₅ Cr] ₂ {C(OEt)CH ₂ PPh ₂ }] (III)	1.07 (t, 3H, OCH ₂ CH ₃), 4.84 (d, 2H, CH ₂), 4.95 (q, 2H, OCH ₂), 2.6 (m, 10H, Ph)
[(CO) ₄ Cr{C(OEt)C(OEt)(Bu)CH ₂ PPh ₂ }] (IV)	1.00 (t, 3H, OCH ₂ CH ₃), 1.1 (m, 9H, Bu) 1.67 (t, 3H, C _{carb} OCH ₂ CH ₃), 2.40 (dd, 1H, CH ₂), 3.10 (dd, 1H, CH ₂), 3.22 (q, 2H, OCH ₂), 5.20 (q, 2H, C _{carb} OCH ₂), 7.5 (m, 10H, Ph)
[(CO) ₄ Cr{C(OEt)C(OEt)CHPPh ₂ }] (V)	1.42 (t, 3H, OCH ₂ CH ₃), 1.65 (t, 3H, C _{carb} OCH ₂ CH ₃), 4.02 (q, 2H, OCH ₂), 5.18 (q, 2H, C _{carb} OCH ₂), 6.30 (s, 1H, CH), 7.5 (m, 10H, Ph)
[(CO) ₄ Cr{C(NH ₂)C(OEt)CHPPh ₂ }] (VI)	1.42 (t, 3H, OCH ₂ CH ₃), 4.08 (2H, OCH ₂), 6.37 (d, 1H, CH), 7.4 (m, 10H, Ph), 1.1 (br, 2H, NH ₂)
[(CO) ₅ W] ₂ {C(OEt)CH(Et)PPh ₂ }] (VII)	0.93 (t, 3H, CH ₂ CH ₃), 1.54 (t, 3H, OCH ₂ CH ₃), 1.9 (m, 2H, CH ₂ CH ₃), 4.9 (m, 1H, CH), 4.94 (q, 2H, OCH ₂), 7.3 (m, 10H, Ph)
[(CO) ₅ Cr{PPh ₂ CH ₂ C(OEt)NH}] (VIII)	1.30 (t, 3H, OCH ₂ CH ₃), 3.57 (d, 2H, CH ₂), 4.07 (q, 2H, OCH ₂), 6.6 (br, 1H, NH), 7.6 (m, 10H, Ph)
[(CO) ₅ W{PPh ₂ CH ₂ C(OEt)NH}] (IX)	0.98 (t, 3H, OCH ₂ CH ₃), 2.05 (q, 2H, OCH ₂), 3.90 (d, 2H, CH ₂), 6.7 (br, 1H, NH), 7.4 (m, 10H, Ph)
[(CO) ₄ Cr{N(i)P}] ^c (X)	0.95 (t, 3H, OCH ₂ CH ₃), 1.2 (m, 9H, Bu), 1.42 (t, 3H, NCOCH ₂ CH ₃), 2.37 (dd, 1H, CH ₂), 3.15 (dd, 1H, CH ₂), 3.25 (q, 2H, COCH ₂), 3.92 (q, 2H, NCOCH ₂), 7.0 (br, 1H, NH), 7.5 (m, 10H, Ph)
[(CO) ₄ Cr{N(ii)P}] ^c (XI)	1.40 (t, 6H, OCH ₂ CH ₃ and NCOCH ₂ CH ₃), 3.95 (q, 4H, OCH ₂ and NCOCH ₂), 4.15 (d, 1H, CH), 7.5 (m, 10H, Ph)

^a Abbreviations: br, broad; d, doublet; dd, doublet of doublets; m, multiplet; s, singlet; t, triplet; q, quartet. ^b Coupling constants, *J*(PCH): I, < 0.5; II, 0; III, 4.5; IV, 8 and 10; V, 0; VI, 2; VII, 4; VIII, 7; IX, 8; X, 6 and 10; XI, 6 Hz. ^c N(i)P = NH=C(OEt)C(OEt)(Bu)CH₂PPh₂; N(ii)P = NH=C(OEt)-C(OEt)=CHPPh₂.

the phosphorus atom in the carbene anion, which increases its nucleophilicity, and the labilizing effect of the oxonium salt [7]. The low yield neutral chromium-containing product derived from I was then formed by acidification on commercial SiO₂, whereas the more unreactive anionic tungsten complex was alkylated to afford



SCHEME 2. Reagent: (i) LiBu.

VII. During the formation of carbene-thioether complexes by the previously mentioned method involving formal CO insertion, the cyclization reaction is very slow when tungsten is central metal. In the present study using II as precursor, no cyclization was observed. Later we established that in the presence of an equimolar amount of PMe_3 which inhibited cyclization, two reactions occurred when I was deprotonated and subsequently alkylated: in one of these the carbene ligand was replaced by PMe_3 to give $[(\text{CO})_5\text{Cr}(\text{PMe}_3)]$ (10%) [7], and in the other the carbene anion was transformed into the complex $[(\text{CO})_5\text{Cr}\{\text{C}(\text{OEt})\text{Pr}\}]$ (58%) [8].

The proposed mechanism for the ring formation in V is given in Scheme 2. It is based on previous observations on insertion reactions into the metal carbene bond [1,3,9]. The neutral product is obtained after further alkylation.

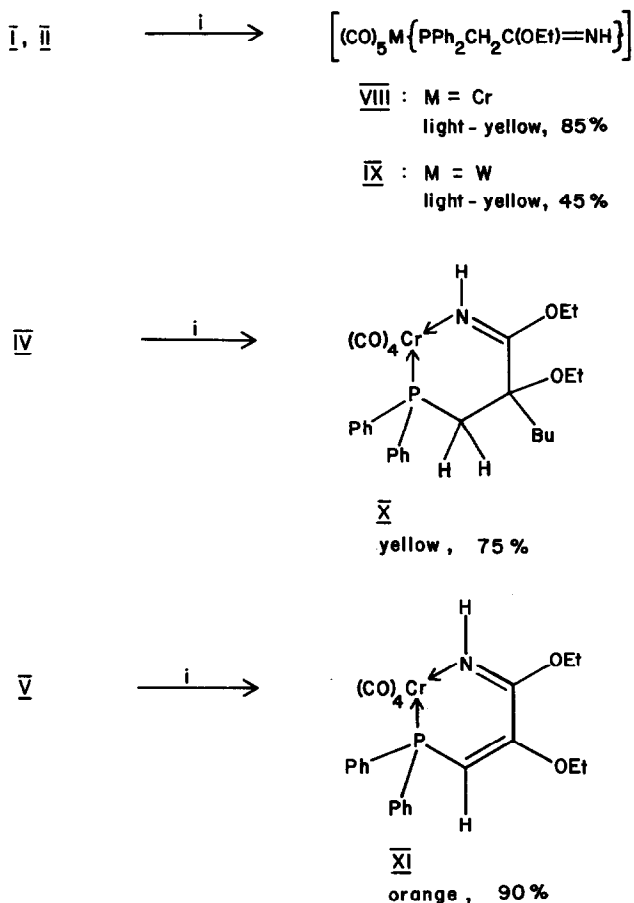
Reaction of carbene complexes with MeNHNH_2

The carbene complexes I, II, IV and V reacted with excess MeNHNH_2 at -80°C to give yellow solutions of the compounds VIII–XI, which were obtained analytically pure after crystallization from ether/hexane at -30°C (Scheme 3). At the low temperature used there was no NMe insertion such as was previously found for a carbene-thioether chelate at -20°C [3]. All the complexes were stable in air and soluble in organic solvents such as hexane, ether, and methylene chloride.

In addition to the initial loss of five carbonyl groups, the pentacarbonyl complexes VIII and IX also underwent another fragmentation in the mass spectrometer by initial loss of HOEt before the five CO ligands and a CNCH_2 group were successively lost. The mass spectra gave no direct information about the coordination mode. The chromium complex gave ions with m/z values corresponding to $[\text{CrPPh}_2]^+$ and $[\text{CrNCCH}_2]^+$. A molecular ion was observed for compound XI, but X had the highest peak at m/z 521 corresponding to the fragment ion $[(\text{CO})_3\text{Cr}\{\text{NH}=\text{C}(\text{OEt})\text{C}(\text{OEt})(\text{Bu})\text{CH}_2\text{PPh}_2\}]^+$.

Spectroscopic characterization data for the new coordinated imidates are listed in Tables 1 and 2. For comparative purposes infrared frequencies for the pentacarbonyl imidate complexes $[(\text{CO})_5\text{M}\{\text{NH}=\text{C}(\text{OEt})\text{C}(\text{OEt})=\text{CS}(\text{CH}_2)_3\text{S}\}]$ $\{\text{M} = \text{Cr} (\text{A}) \text{ or } \text{W} (\text{B})\}$ as well as the disubstituted carbonyl complex $[(\text{CO})_4\text{Cr}\{\text{NH}=\text{C}(\text{OEt})\text{C}(\text{OEt})=\text{CS}(\text{CH}_2)_3\text{S}\}]$ (C), are also included in Table 1.

The different frequency and intensity patterns of VIII and IX compared to those of A and B gave the first indication of preferred P rather than N coordination in VIII and IX. The lower values obtained for the tetracarbonyl complexes after NH insertion indicate that more negative charge is transferred to the central metal and

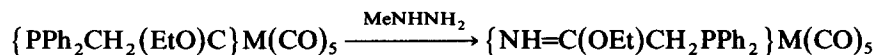
SCHEME 3. Reagent: (i) MeNHNH_2 .

subsequently to the carbonyls, by the imidate-phosphine bidentate ligands than by the carbene-phosphine chelate rings.

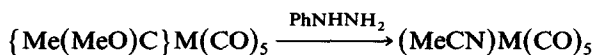
Our assignment of P coordination in the pentacarbonyl complexes VIII and IX was finally based on the relatively high coupling constants ($J(\text{PCH})$ respectively 7 and 8 Hz) exhibited by these complexes compared to the low values (< 0.5 Hz) in the pentacarbonyl P-containing carbene complexes I and II. Pidcock [10] reported values larger than 6 Hz in a variety of monodentate phosphine coordination complexes. On NH addition to the carbene complexes and P coordination, a downfield shift of the PCH_2 resonance in the ^1H NMR spectra occurred (I: δ 4.13; VIII: δ 3.57 ppm).

The ^1H NMR spectra of the tetracarbonyl complexes did not change substantially after NH insertion into the metal-carbene bond. The expected number of resonances and correct relative intensities were observed (Table 2).

The reaction



is completely unexpected for the pentacarbonyl complexes, especially in the light of the following reaction reported by Fischer and Aumann [4]:



The same authors observed formal NH insertion on treatment of carbene complexes with hydroxylamine. We also treated $[(\text{CO})_5\text{Cr}\{\text{C}(\text{OEt})\text{Ph}\}]$ with MeNHNH_2 under the conditions used for I and II; six yellow products were formed in low yields and were not isolated. Later we found that reaction of terminal pentacarbonyl carbene complexes with $\text{Ph}_2\text{S}=\text{NH}$ provided an easy and quantitative procedure for NH insertion into the metal–carbene bond. The results will be described elsewhere.

Crystal and molecular structure of $[(\text{CO})_4\text{Cr}\{\text{C}(\text{NH}_2)\text{C}(\text{OEt})=\text{CHPh}_2\}]$ (VI)

The monoclinic crystals of VI contain monomeric units separated by normal Van der Waals distances. The molecular configuration was as expected, and Fig. 1 shows the molecular geometry and explains the atomic labeling scheme. Bond lengths and angles are given in Table 3. The short C(5)–C(6) distance of 1.338(7) Å is to be compared to an interatomic distance of 1.500(7) Å between C(6) and C(7), and shows the presence of a localized double bond between C(5) and C(6). The sp^2 overlap with phosphorus (C(5)–P) results in a shorter bond (1.791(5) Å) than that between an sp^3 carbon atom and phosphorus (1.869(9) Å) [13]. The most pronounced deviation from idealised octahedral symmetry around the chromium atom is shown by the C(carbene)–Cr–P angle, which has a value of 79.3(1)°. The Cr–C(aminocarbene) length of 2.067(5) Å compares with a 2.064(8) Å metal–carbene carbon separation in the disubstituted aminocarbene carbonyl complex $[(\text{CO})_4\text{Cr}\{\text{C}(\text{NH}_2)\text{Ph}\}(\text{CNBu}^1)]$ [14]. A final notable feature is the agreement between the distances (Table 4) around the chromium atom and those reported for the disubstituted carbonyl complex $[(\text{CO})_4\text{Cr}(\text{diphos})]$ (diphos = $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$) [13]. This again [14] emphasizes the similarity in bonding characteristics between carbene ligands of the Fischer-type and phosphine ligands.

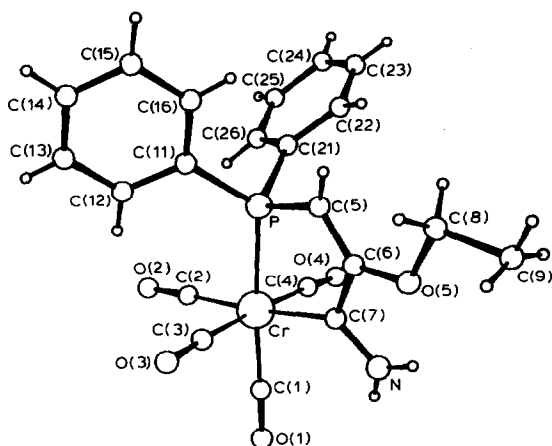


Fig. 1. The $[(\text{CO})_4\text{Cr}\{\text{C}(\text{NH}_2)\text{C}(\text{OEt})=\text{CHPh}_2\}]$ molecule, with the crystallographic labels indicated. Hydrogens are named after the atoms to which they are bonded.

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) FOR COMPOUND VI

Cr–C(1)	1.851(5)	C(5)–C(6)	1.338(7)
Cr–C(2)	1.853(5)	C(6)–C(7)	1.500(7)
Cr–C(3)	1.886(5)	C(8)–C(9)	1.521(8)
Cr–C(4)	1.886(5)	C(11)–C(12)	1.386(7)
Cr–P	2.352(1)	C(11)–C(16)	1.390(7)
Cr–C(7)	2.067(5)	C(12)–C(13)	1.395(8)
C(1)–O(1)	1.161(7)	C(13)–C(14)	1.376(10)
C(2)–O(2)	1.163(6)	C(14)–C(15)	1.364(10)
C(3)–O(3)	1.153(6)	C(15)–C(16)	1.384(8)
C(4)–O(4)	1.154(7)	C(21)–C(22)	1.386(8)
C(6)–O(5)	1.360(6)	C(21)–C(26)	1.387(8)
C(7)–N	1.314(7)	C(22)–C(23)	1.400(9)
O(5)–C(8)	1.452(6)	C(23)–C(24)	1.394(11)
P–C(5)	1.791(5)	C(24)–C(25)	1.362(11)
P–C(11)	1.837(5)	C(25)–C(26)	1.394(9)
P–C(21)	1.840(5)		
C(1)–Cr–C(2)	91.2(2)	P–C(11)–C(12)	118.9(4)
C(1)–Cr–C(3)	88.6(2)	P–C(11)–C(16)	124.0(4)
C(1)–Cr–C(4)	89.0(2)	P–C(21)–C(22)	120.3(4)
C(1)–Cr–P	174.1(2)	P–C(21)–C(26)	121.6(4)
C(1)–Cr–C(7)	94.9(2)	O(5)–C(8)–C(9)	107.9(5)
C(2)–Cr–C(3)	90.4(2)	C(5)–C(6)–C(7)	118.9(4)
C(2)–Cr–C(4)	92.3(2)	C(5)–C(6)–O(5)	127.4(4)
C(2)–Cr–P	94.7(2)	C(5)–P–C(21)	103.7(2)
C(2)–Cr–C(7)	173.8(2)	C(5)–P–C(11)	104.9(2)
C(3)–Cr–C(4)	176.5(2)	C(6)–O(5)–C(8)	118.2(4)
C(3)–Cr–P	91.4(2)	C(6)–C(7)–N	112.0(4)
C(3)–Cr–C(7)	91.3(2)	C(7)–C(6)–O(5)	113.7(4)
C(4)–Cr–P	90.7(2)	C(11)–C(12)–C(13)	120.6(5)
C(4)–Cr–C(7)	86.3(2)	C(11)–C(16)–C(15)	122.6(5)
P–Cr–C(7)	79.3(1)	C(11)–P–C(21)	100.5(2)
O(1)–C(1)–Cr	178.1(4)	C(12)–C(11)–C(16)	117.1(4)
O(2)–C(2)–Cr	178.3(5)	C(12)–C(13)–C(14)	120.3(6)
O(3)–C(3)–Cr	176.9(4)	C(13)–C(14)–C(15)	120.3(6)
O(4)–C(4)–Cr	177.1(5)	C(14)–C(15)–C(16)	119.1(6)
N–C(7)–Cr	126.5(4)	C(21)–C(22)–C(23)	120.5(5)
C(6)–C(7)–Cr	121.4(3)	C(21)–C(26)–C(25)	122.4(6)
C(5)–P–Cr	104.2(2)	C(22)–C(21)–C(26)	143.8(5)
C(11)–P–Cr	118.9(2)	C(22)–C(23)–C(24)	119.4(6)
C(21)–P–Cr	122.6(2)	C(23)–C(24)–C(25)	121.1(7)
P–C(5)–C(6)	114.7(4)	C(24)–C(25)–C(26)	118.6(6)

TABLE 4

COMPARISON OF MOLECULAR PARAMETERS OF $[(\text{CO})_4\text{Cr}\{\text{C}(\text{NH}_2)\text{C}(\text{OEt})=\text{CHPh}_2\}]$ (VI) AND $[(\text{CO})_4\text{Cr}(\text{diphos})]$

	Bond lengths (Å)			
	Cr–P	Cr–C(<i>trans</i>)	Cr–C(<i>cis</i>)	P–C
(VI)	2.35(1)	1.85(1)	1.89(1)	1.83(av)
$[(\text{CO})_4\text{Cr}(\text{diphos})]$	2.36(av)	1.83(1)	1.88(1)	1.83(1)

Experimental

The Schlenk techniques used and instrumentation employed in this work, have been described previously [11]. $[(\text{CO})_5\text{Cr}\{\text{C}(\text{OEt})\text{Me}\}]$ was prepared by a literature procedure [15]. Commercial chlorodiphenylphosphine and methylhydrazine were used without purification.

Preparation of the pentacarbonylcarbene complexes, $[(\text{CO})_5M\{\text{C}(\text{OEt})\text{CH}_2\text{PPh}_2\}]$ ($M = \text{Cr or W}$)

The synthesis of the chromium complex I is described in detail. BuLi (15.0 mmol) in hexane was added dropwise to $[(\text{CO})_5\text{Cr}\{\text{C}(\text{OEt})\text{Me}\}]$ (3.96 g, 15.0 mmol) in 100 cm³ tetrahydrofuran (THF) at -60°C . After 5 min an equimolar amount of Ph_2PCl (3.31 g) was added in one batch to the mixture, which was then immediately subjected to flash chromatography on a silica gel column (-10°C) with THF as eluant. The first orange zone was collected and the solvent removed under reduced pressure. The resulting oil was chromatographed again with hexane/ CH_2Cl_2 (4/1) as eluant. Evaporation of the solvent afforded 3.63 g (54% yield) of an orange oil (I). This slowly decomposed, and was characterized spectrometrically.

The other pentacarbonyltungsten complex (II) was prepared similarly. It was isolated as orange crystals in a yield of 69% after crystallization from ether/hexane (1/5) at -30°C . M.p. $37-38^\circ\text{C}$. Anal. Found: C, 43.51; H, 2.73; P, 5.21. $\text{WC}_{21}\text{H}_{17}\text{O}_6\text{P}$ calcd.: C, 43.47; H, 2.95; P, 5.34%.

Deprotonation and subsequent alkylation of compounds I and II

LiBu (8 mmol in hexane) was added to a cold (-60°C) solution of $[(\text{CO})_5\text{Cr}\{\text{C}(\text{OEt})\text{CH}_2\text{PPh}_2\}]$ (3.36 g, 7.50 mmol) in THF (50 cm³). The solution was allowed to warm slowly to room temperature, the solvent was removed, and alkylation with $[\text{Et}_3\text{O}][\text{BF}_4]$ (monitored by TLC) was carried out in CH_2Cl_2 . The mixture was washed through SiO_2 with CH_2Cl_2 and the dried residue was chromatographed on silica gel (-10°C) with hexane/ CH_2Cl_2 (4/1) as eluant. Consecutive yellow, brown and red fractions were separately collected and the solvent was removed under reduced pressure. Crystallization of the first solid obtained (ether/hexane, 1/5) afforded 0.28 g (10% based on I) of III as yellow needlelike crystals. M.p. $99-101^\circ\text{C}$. Anal. Found: Cr, 16.2; C, 48.69; H, 2.75; O, 28.0; P, 4.71. $\text{CrC}_{26}\text{H}_{17}\text{O}_{11}\text{P}$ calcd.: Cr, 16.24; C, 48.77; H, 2.68; O, 27.48; P, 4.84%. Crystallization of the second residue afforded 1.31 g (33%) of IV as brown crystals. M.p. $120-122^\circ\text{C}$. Anal. Found: C, 60.53; H, 5.84; P, 5.63. $\text{CrC}_{27}\text{H}_{31}\text{O}_6\text{P}$ calcd.: C, 60.67; H, 5.85; P, 5.79%. The last fraction contained V as an oily substance which was precipitated from ether on addition of hexane (0.95 g, 27%). The red oil was dissolved in 20 cm³ ether and NH_3 was bubbled through the solution for 5 min. After removal of the solvent, recrystallization from ether/hexane (1/5) furnished stable red crystals of VI (0.81 g, 90%). M.p. 100°C (dec.). Anal. Found: C, 56.48; H, 4.27; N, 2.93; $\text{CrC}_{21}\text{H}_{18}\text{NO}_5\text{P}$ calcd.: C, 56.38; H, 4.06; N, 3.13%.

A similar treatment of II using 2.5 g (4.31 mmol) afforded only one isolable product (VII), as yellow needle-like crystals (0.56 g, 13%). M.p. $122-124^\circ\text{C}$. Anal. Found: C, 36.40; H, 2.32; P, 2.99. $\text{W}_2\text{C}_{28}\text{H}_{21}\text{O}_{11}\text{P}$ calcd.: C, 36.08; H, 2.27; P, 3.32%.

Reaction of carbene complexes with MeNHNH₂

An excess (5 mmol) of MeNHNH₂ was added slowly to a cooled (−80°C) solution of [(CO)₅Cr{C(OEt)CH₂PPh₂}] (1.25 g, 2.8 mmol) in 100 ml of ether. The solution turned yellow immediately. It was stirred for 5 min and the solvent was then removed in vacuo. Crystallization from ether/hexane (5/1) afforded light yellow crystals of VIII (1.10 g, 85%). Pure crystals of IX, X and XI were obtained in the same fashion.

VIII. M.p. 66–67°C. Anal. Found: C, 54.32; H, 4.01; N, 2.93. CrC₂₁H₁₈NO₆P calcd.: C, 54.44; H, 3.92; N, 3.02%.

IX. Light yellow crystals, yield 45%. M.p. 120–122°C. Anal. Found: C, 42.31; H, 3.10; N, 2.51. WC₂₁H₁₈NO₆P calcd.: C, 42.38; H, 3.05; N, 2.35%.

X. Yellow crystals, yield 75%. M.p. 140°C (dec.). Anal. Found: C, 58.93; H, 5.89; N, 2.54. CrC₂₇H₃₂NO₆P calcd.: C, 59.01; H, 5.84; N, 2.55%.

XI. Orange crystals, yield 90%. M.p. 145–147°C. Anal. Found: C, 56.23; H, 4.55; N, 2.85. CrC₂₃H₂₂NO₆P calcd.: C, 56.22; H, 4.51; N, 2.85%.

Structure determination

Prismatic orange crystals of VI were grown by keeping an ether/hexane solution at −30°C. The crystal used for the structure analysis had approximate dimensions 0.2 × 0.05 × 0.05 mm. The intensity data were corrected for Lorentz and polarization effects but not for absorption. The crystal data and details of the data collection are given in Table 5.

TABLE 5

CRYSTALLOGRAPHIC DATA FOR [(CO)₄Cr{C(NH₂)C(OEt)=CHPPh₂}] (VI)

Unit cell parameters

Crystal system: monoclinic

Space group: *P*2₁/*c*

a 12.55(1) Å

b 13.50(1) Å

c 12.83(1) Å

β 90.2(1)°

V 2174 Å³

Formula: C₂₁H₁₈NO₅PCr

Molecular wt.: 447.37

Z = 4

D(calc.) 1.37 g cm^{−3}

μ(Mo-*K*_α) 5.8 cm^{−1}

Data collection

Diffractionmeter: Philips PW 1100

Radiation: Mo-*K*_α (λ 0.7107 Å)

Monochromator: Graphite

Reflections measured: 3155 (θ < 23°)

Reflections with *I* < 2σ: 821

Reflections with *I* > 0: 2956

Scan type: coupled (ω–2θ)

Scan width: θ 1.2°

Scan speed: θ 0.04° s^{−1}

Standards: 3 remeasured every 60 min no significant drift observed.

TABLE 6
ATOMIC COORDINATES FOR COMPOUND VI

Non-hydrogen coordinates ($\times 10^4$) with e.s.d.'s			
Atom	x	y	z
Cr	7330(1)	-296(1)	1264(1)
C(1)	7116(4)	-1567(4)	1763(4)
O(1)	6976(3)	-2353(3)	2104(3)
C(2)	7470(4)	191(4)	2607(4)
O(2)	7555(3)	473(3)	3460(3)
C(3)	5844(4)	-94(4)	1316(4)
O(3)	4934(3)	-3(3)	1383(3)
C(4)	8800(4)	-573(4)	1171(4)
O(4)	9689(3)	-784(4)	1119(4)
P	7587(1)	1250(1)	0457(1)
C(5)	7751(4)	955(4)	-894(4)
C(6)	7561(3)	7(3)	-1138(3)
C(7)	7242(4)	-696(4)	-289(4)
N	6938(4)	-1559(3)	-661(4)
O(5)	7608(3)	-419(2)	-2097(2)
C(8)	7872(6)	205(5)	-2981(4)
C(9)	7680(6)	-392(5)	-3969(4)
C(11)	6503(3)	2164(3)	488(4)
C(12)	6131(4)	2487(4)	1445(4)
C(13)	5328(5)	3201(5)	1503(6)
C(14)	4881(5)	3579(5)	606(6)
C(15)	5214(5)	3255(5)	-346(6)
C(16)	6013(4)	2550(4)	-396(5)
C(21)	8736(4)	2050(4)	751(4)
C(22)	8970(5)	2852(4)	117(5)
C(23)	9866(5)	3442(5)	318(6)
C(24)	10529(6)	3209(6)	1156(7)
C(25)	10311(5)	2427(6)	1793(6)
C(26)	9408(5)	1858(5)	1587(5)

Anisotropic thermal parameters a ($\text{\AA}^2 \times 10^3$) with e.s.d.'s						
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr	34(1)	33(1)	28(1)	3(1)	-6(1)	3(1)
C(1)	54(3)	44(4)	42(3)	4(3)	-7(3)	5(3)
O(1)	99(3)	45(3)	82(3)	28(2)	-5(3)	-1(2)
C(2)	63(4)	46(3)	34(3)	4(3)	-6(3)	7(3)
O(2)	134(4)	99(4)	39(3)	-15(2)	-17(3)	10(3)
C(3)	45(3)	46(3)	42(3)	15(3)	3(2)	1(3)
O(3)	38(2)	99(4)	111(4)	36(3)	5(2)	6(2)
C(4)	53(4)	57(4)	37(3)	4(3)	-2(3)	6(3)
O(4)	42(3)	130(4)	114(4)	6(3)	-2(3)	23(3)
P	34(1)	31(1)	29(1)	-2(1)	-5(1)	-2(1)
C(5)	39(3)	35(3)	30(3)	2(3)	-2(2)	-6(3)
C(6)	34(3)	36(3)	21(3)	-3(2)	0(2)	1(2)
C(7)	35(3)	30(3)	34(3)	-3(3)	-5(2)	0(2)
N	102(4)	42(3)	37(3)	1(3)	-4(3)	-22(3)
O(5)	64(2)	40(2)	30(2)	-5(2)	1(2)	-3(2)
C(8)	70(5)	67(4)	31(3)	1(3)	5(3)	-10(4)
C(9)	150(7)	85(5)	25(4)	-15(4)	-2(4)	-4(5)
C(11)	38(3)	32(3)	34(3)	-4(2)	-5(2)	-3(2)

TABLE 6 (continued)

Anisotropic thermal parameters a ($\text{\AA}^2 \times 10^3$) with e.s.d.'s						
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(12)	61(4)	63(4)	47(4)	-12(3)	-10(3)	21(3)
C(13)	68(4)	69(4)	81(5)	-28(4)	8(4)	20(4)
C(14)	46(4)	41(4)	129(6)	-3(4)	-10(4)	17(3)
C(15)	58(4)	70(5)	98(5)	12(4)	4(4)	26(4)
C(16)	63(4)	71(4)	47(4)	8(3)	0(3)	18(3)
C(21)	37(3)	35(3)	37(3)	-8(3)	-4(3)	-3(3)
C(22)	58(4)	47(4)	70(5)	5(3)	-11(3)	-17(3)
C(23)	74(4)	47(3)	110(5)	0(4)	8(4)	-30(4)
C(24)	60(5)	77(5)	132(7)	-34(4)	-25(5)	-31(4)
C(25)	76(5)	75(5)	110(6)	-6(5)	-33(4)	-31(4)
C(26)	66(4)	65(4)	63(4)	3(3)	-23(3)	-23(3)
H coordinates ($\times 10^3$) with e.s.d.'s b						
Atom	x	y	z			
H(5)	800(4)	147(4)	130(4)			
N(N1)	689(4)	-160(4)	-126(4)			
H(N2)	671(5)	-202(4)	-25(4)			
H(8a)	862(4)	40(4)	-298(4)			
H(8b)	727(4)	78(4)	-291(4)			
H(9a)	672(4)	-55(4)	-384(4)			
H(9b)	816(4)	1(4)	-441(4)			
H(9c)	746(4)	-7(4)	-458(4)			
H(12)	649(4)	217(4)	202(4)			
H(13)	501(4)	338(4)	217(4)			
H(14)	438(4)	404(4)	66(4)			
H(15)	519(4)	363(4)	-127(4)			
H(16)	624(4)	241(4)	-105(4)			
H(22)	851(4)	306(4)	-50(4)			
H(23)	996(4)	397(4)	-7(4)			
H(24)	1109(4)	365(4)	126(4)			
H(25)	1081(4)	207(4)	241(4)			
H(26)	915(4)	135(4)	210(4)			

a The form of the expression is $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + \dots)]$. b The H atoms were refined with a common isotropic temperature factor of $0.08 \text{ \AA}^2$.

The crystal structure was solved by the heavy-atom method and refined by full-matrix least-squares. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = (\sigma(F_o))^{-2}$. All the hydrogen atoms were located in difference-Fourier syntheses and refined with a common isotropic thermal parameter of $0.08 \text{ \AA}^2$. Refinement converged with $R = 0.067$ and $R_w = 0.050$, using the 2956 data with positive intensities. A final difference map showed no significant features. The calculations were carried out with the SHELX-76 [16] crystallographic programme package. Positional and thermal parameters are listed in Table 6. A table of observed and calculated structure factor amplitudes is available upon request from G.J.K.

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References

- 1 R.G. Raubenheimer, S. Lotz, H.W. Viljoen and A.A. Chalmers, *J. Organomet. Chem.*, 152 (1978) 73.
- 2 H.P. Abicht and K. Issleib, *J. Organomet. Chem.*, 132 (1977) 327.
- 3 S. Lotz, H.G. Raubenheimer, H.W. Viljoen and J.C. Viljoen, *S. Afr. J. Chem.*, 36 (1983) 13.
- 4 E.O. Fischer and R. Aumann, *Chem. Ber.*, 101 (1968) 963.
- 5 C.P. Casey and W.R. Brunsvold, *J. Organomet. Chem.*, 102 (1975) 175.
- 6 P.S. Braterman, *Struct. and Bonding*, 26 (1976) 1.
- 7 J.A. Connor, E.M. Jones and G.K. Mc Ewen, *J. Organomet. Chem.*, 43 (1972) 357.
- 8 E.O. Fischer and L. Knauss, *Chem. Ber.*, 103 (1970) 1262.
- 9 H.G. Raubenheimer, S. Lotz, H.E. Swanepoel, H.W. Viljoen and J.C. Rautenbach, *J. Chem. Soc., Dalton Trans.*, (1979) 1701.
- 10 A. Pidcock, *J. Chem. Soc., Chem. Commun.*, (1968) 92.
- 11 H.G. Raubenheimer, G.J. Kruger and H.W. Viljoen, *J. Chem. Soc., Dalton Trans.*, (1985) 1963.
- 12 D.C. Nelson in S. Patai (Ed.), *The Chemistry of Amidines and Imidates*, Interscience Publishers, New York, 1975.
- 13 M.J. Bennet, F.A. Cotton and M.D. La Prade, *Acta Cryst.*, B27 (1971) 1899.
- 14 H.G. Raubenheimer, G.J. Kruger, H.W. Viljoen and A. Lombard, *J. Chem. Res. (S)*, (1982) 202.
- 15 R. Aumann and E.O. Fischer, *Angew. Chem., Int. Ed. Engl.*, 6 (1967) 879.
- 16 G.M. Sheldrick, in H. Schenck, R. Olthoff-Hazekamp, H. van Koningsveld and G.C. Bassi (Eds.), *Computing in Crystallography*, University Press, Delft, 1978.