N,N-Diethylcarbamato tertiary phosphine complexes as precursors to carbonato and carbamoyl platinum(II) derivatives ‡

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The complexes cis-Pt$(O_2CNEt_2)_2(PR_3)_2$ (R = Ph, Et) and Pt$(O_2CNEt_2)_2$(DPPE) [DPPE = 1,2-bis(diphenylphosphino)ethane] were prepared by the reaction of the corresponding phosphino-chloro complexes of platinum with Ag(O_2CNEt_2). The new N,N-diethylcarbamato complexes are excellent precursors for the high-yielding preparation of the corresponding carbonato derivatives Pt$(CO_3)(PR_3)_2$ or Pt(CO_3)(DPPE) by reaction with a stoichiometric amount of water. The carbamato complex cis-Pt$(O_2CNEt_2)_2(PPh_3)_2$ reacts with CO producing the carbamoyl derivative cis-Pt$[C(O)NEt_2]_2(PPh_3)_2$. The chloro-carbamoyl complex, prepared by reacting cis-PtCl$_2(PPh_3)_2$ with NHEt$_2$ and CO, and recrystallized from toluene as the solvated species $trans$-PtCl$[C(O)NEt_2](PPh_3)_2$·2 C$_6$H$_5$Me has been structurally characterized.

Introduction

Several metal N,N-dialkylcarbamato complexes have been prepared in recent years with an important contribution from our laboratories,[1–5] and the reactivity of these compounds has been studied. Protic reagents usually attack these derivatives with evolution of CO_2. Formation of sulfido-,[6] μ-oxo-,[7] acetato-,[8] acetylacetonato-[9] or halogeno-[6b,8,9] complexes, by reaction with H_2S, water, acetic acid, acetylacetone or hydrogen halides, respectively, exemplifies this type of reactivity. In addition, acidic silanol functionalities on amorphous silica react with formation of surface-bonded silicato metal complexes.[3–5]

The reactivity of N,N-dialkylcarbamato metal complexes towards CO was studied for some copper(I) and silver(I) derivatives of this class:[2] with copper, the reversible formation of a carbonyl-carbamato derivative, in equilibrium with the precursor, was established, while the silver complex undergoes reduction to metal with concomitant mono- or bi-electronic oxidation of CO to oxamide $(CONEt_2)_2$ or to carbamic anhydride $O(CONEt_2)_2$, respectively, depending on the reaction conditions. The intermediate formation of carbamoyl silver complexes was suggested.

N,N-Dialkylcarbamato complexes of platinum(II) have already been reported and $trans$-Pt$(O_2CNEt_2)_2(NHEt_2)_2$ was found[4] to be isotypical with the analogous palladium derivative[10] and was used for platinum implantation on silica.[4]

In this paper some new N,N-dialkylcarbamato complexes of platinum(II) with tertiary phosphines as ancillary ligands are reported, together with their use as precursors to carbonato complexes, by reaction with water, or to bis(carbamoyl) complexes, by reaction with CO.

Results and discussion

Syntheses and characterization

The platinum N,N-diethylcarbamato complexes were prepared using the platinum complexes cis-PtCl$_2$P*$_2$ [P*$_2$ = $(PPh_3)_2$, $(PEt_3)_2$ or DPPE] as starting materials. The triethylphosphine derivative cis-PtCl$_2(PEt_3)_2$ was prepared from cis-PtCl$_2(CO)_2$ and PEt$_3$ in toluene, see eqn. (1).

$$cis\text{-PtCl}_2(CO)_2 + 2\,PEt_3 \longrightarrow cis\text{-PtCl}_2(PEt_3)_2 + 2\,CO \quad (1)$$
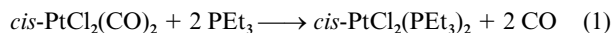
Under these conditions, an equilibrium between the cis and the more soluble $trans$ isomer is achieved; in the presence of CO, see eqn. (2), the partially soluble cis isomer can thus be

$$cis\text{-PtCl}_2(PEt_3)_2 \rightleftharpoons trans\text{-PtCl}_2(PEt_3)_2 \quad (2)$$
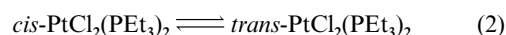
obtained in yields as high as 75%, if care is taken to use limited amounts of solvent.

The reaction of the cis-phosphino-chloro complexes of platinum with Ag(O_2CNEt_2)[2,11] affords cis-Pt$(O_2CNEt_2)_2$P*$_2$, see eqn. (3). The use of the silver derivative as chloride scavenger

$$cis\text{-PtCl}_2P^*_2 + 2\,Ag(O_2CNEt_2) \longrightarrow$$
$$2\,AgCl + cis\text{-Pt}(O_2CNEt_2)_2P^*_2 \quad (3)$$
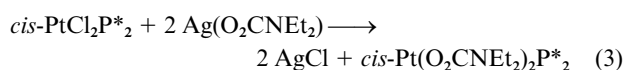
was dictated by the failure of carbamate to substitute the chloride using the NHEt$_2$/CO$_2$ system. The high Pt–Cl bond energy[12] is probably responsible for this behaviour; in fact, chloride substitution in cis-PtCl$_2$P*$_2$ should be kinetically feasible in view of the high $trans$ effect of the tertiary phosphine ligands.

All three carbamato derivatives are microcrystalline colourless products and are very sensitive to moisture being converted to the corresponding carbonato complexes (see below). They were characterized by determining the CO_2 content upon treatment with acetic acid in toluene, and by IR and NMR spectroscopies.

Table 1 ¹H and ¹³C NMR spectra of *cis*-Pt(O₂CNEt₂)₂P*₂, Pt(CO₃) (PEt₃)₂, *cis*-Pt[C(O)NEt₂]₂(PPh₃)₂ and *trans*-PtCl[C(O)NEt₂(PPh₃)₂[a]

	¹H	¹³C
cis-Pt(O₂CNEt₂)₂(PPh₃)₂	1.1 (t, CH_3CH₂N); 3.2 (q, CH₃CH_2N); 6.9 (m) and 7.8 m (aromatic protons)[b]	14.9 s (CH_3CH₂N); 42.1 s (CH₃CH_2N); 128.0 m, 130.3 s and 135.4 m (aromatic carbons); 161.4 s (CO₂N)[b]
cis-Pt(O₂CNEt₂)₂(DPPE)	0.9 t (CH_3CH₂N); 2.1 m[16] (PCH_2CH₂P); 3.0 q (CH₃CH_2N); 7.4–8.0 m (aromatic protons)[c]	
cis-Pt(O₂CNEt₂)₂(PEt₃)₂	0.9 m (CH_3CH₂P); 1.3 t (CH_3CH₂N); 1.5 m (CH₃CH_2P); 3.5 q (CH₃CH_2N)[b]	7.9(CH_3CH₂P; J_{Pt-C} = 24.8); 14.9 s (CH_3CH₂N); 15.2 m (CH₃CH_2P); 41.8 s (CH₃CH_2N); 161.3 (Δ$v_{1/2}$ = 6.5 Hz)[b]
Pt(CO₃)(PEt₃)₂	1.2 m (CH_3CH₂P); 1.8 m (CH₃CH_2P)[c]	8.2 (CH_3CH₂P, J_{Pt-C} = 25.3); 16.1 m (CH₃CH_2P); 168.1 t (O₃C, J_{P-C} = 3.7, J_{Pt-C} = 60.0)[c]
cis-Pt[C(O)NEt₂]₂(PPh₃)₂	0.8 t and 1.0 t (CH_3CH₂N); 2.1 m, 2.7 m, 3.2 m and 4.7 m (CH₃CH_2N); 7.1–7.5 m (aromatic protons)[d]	14.1 s and 14.2 s (CH_3CH₂N); 38.8 (J_{Pt-C} = 18) and 44.0 (J_{Pt-C} = 27) (CH₃CH_2N); 127.3 m, 129.3 s and 134.5 m (aromatic carbons); 187.3 dd ($J_{C-P\ trans}$ = 127, $J_{C-Pt\ cis}$ = 15.2, J_{Pt-C} = 1140) (C(O)NEt₂)[e]
trans-PtCl[C(O)NEt₂](PPh₃)₂	0.5 t and 0.9 t (CH_3CH₂N); 2.6 q and 4.0 q (CH₃CH_2N); 7.7 m and 8.1 m (aromatic protons)[d]	13.7 s and 14.1 s (CH_3CH₂N); 39.7 (J_{Pt-C} = 19.3) and 43.8 (J_{Pt-C} = 35) (CH₃CH_2N); 128.3 m, 130.6 s and 135.3 m (aromatic carbons); 168.4 t (J_{Pt-C} = 1127; J_{Pt-C} = 5.5) (C(O)NEt₂)[e]

[a] δ in ppm; from SiMe₄ (*J*/Hz). [b] In C₆D₆. [c] In CD₂Cl₂. [d] In CDCl₃. [e] In CH₂Cl₂ + C₆D₆.

Table 2 ³¹P and ¹⁹⁵Pt NMR spectra of *cis*-Pt(O₂CNEt₂)₂P*₂, Pt-(CO₃)P*₂, *cis*-Pt[C(O)NEt₂]₂(PPh₃)₂ and *trans*-PtCl[C(O)NEt₂](PPh₃)₂[a]

	³¹P	¹⁹⁵Pt (J_{Pt-P})
cis-Pt(O₂CNEt₂)₂(PPh₃)₂	8.0[b]	−4026 t (3850)[b]
cis-Pt(O₂CNEt₂)₂(DPPE)	31.1[c]	−4259 t (3800)[c]
cis-Pt(O₂CNEt₂)₂(PEt₃)₂	1.3[b]	−4125 t (3680)[b]
Pt(CO₃)(PPh₃)₂	8.6[c]	−4066 t (3700)[d]
Pt(CO₃)(DPPE)	34.2[c]	−4360 t (3520)[c]
Pt(CO₃)(PEt₃)₂	4.9[c]	−4234 t (3460)[d]
cis-Pt[C(O)NEt₂]₂(PPh₃)₂	14.6[b]	−4405 t (1790)[b]
trans-PtCl[C(O)NEt₂](PPh₃)₂	22.0[c]	−4189 t (3300)[d]

[a] δ in ppm: from 85% H₃PO₄ for ³¹P and H₂PtCl₆ in D₂O for ¹⁹⁵Pt (*J*/Hz). [b] In C₆D₆. [c] In CD₂Cl₂. [d] In CDCl₃.

The IR spectra of the carbamato complexes were always contaminated by the bands due to the carbonato derivatives because of the fast hydrolysis during the preparation of the mulls in spite of the precautions taken. The bands due to the carbonato group were subtracted, once their position had been established by preparation of and comparision with authentic samples (see below). The carbamato complexes are characterized by an intense band in the 1600–1560 cm⁻¹ region associated with the O₂CNEt₂ ligand, in agreement with the literature data for the non-homoleptic derivatives of platinum(II) *trans*-PtH(O₂CNHPh)(PEt₃)₂[13a] and *trans*-PtPh(O₂CNH₂)(PCy₃)₂ reporting carbamato bands at 1620 cm⁻¹.[13b]

The NMR spectra, see ¹H, ¹³C, ³¹P and ¹⁹⁵Pt data in Tables 1 and 2, support the proposed composition and structure of the compounds.

The ¹³C resonances of the O₂CN carbon are at about δ 160, as usually found in diamagnetic *N,N*-dialkylcarbamato complexes.[1b,2,3] The observation of single methyl and methylene resonances at room temperature is attributed to free rotation about the O₂C–NEt₂ bond. The ¹⁹⁵Pt resonances are in the range typical for platinum(II) derivatives[14] and the Pt–P coupling constants (about 3800 Hz) are in agreement with the *cis*-structure of the products.[15]

Reactivity

The *N,N*-dialkylcarbamato complexes are extremely moisture-sensitive as is evidenced by their ready conversion into carbonato complexes, Pt(CO₃)P*₂, in good yields. Molecular platinum carbonato derivatives have been described in the literature: they have been most frequently encountered serendipitously, by contact of some precursors with air and/or moisture. For example, Pt(CO₃)(P^{i}Pr₃)₂ resulted[17c] from an attempt to crystallize the corresponding hydride; Pt(CO₃)(PPh₃)₂ was obtained[17a,e] in an attempted synthesis of PtH₂(PPh₃)₂, while Pt(CO₃)(PEt₃)₂ was produced during the recrystallization of *trans*-PtH(CH₂CN)-(PEt₃)₂.[17d] More recently, the compound Pt(CO₃)(PMe₃)₂·2H₂O was obtained[17f] by exposure to air (specifically, to carbon dioxide) of the precursor *cis*-Pt(OH)₂(PMe₃)₂·nH₂O; moreover, carbonato complexes of platinum(II) were prepared from the corresponding chloride by treatment with Ag₂CO₃ in the presence of water in dichloromethane as medium.[17g]

Metal carbamato complexes usually undergo partial hydrolysis producing oxo[7] rather than carbonato derivatives with some exceptions, as for instance in the case of silver.[2] It is reasonable to assume that the formation of metal carbonato complexes is associated with the relatively strong basicity of the hydroxide or oxide, which are presumably the primary products of the hydrolytic process. The reaction of toluene solutions of *cis*-Pt(O₂CNEt₂)₂P*₂ with the stoichiometric amount of water, see eqn. (4), dissolved in THF, gave good to excellent yields

$$Pt(O_2CNEt_2)_2P^*_2 + H_2O \longrightarrow$$
$$Pt(CO_3)P^*_2 + 2\ NHEt_2 + CO_2 \quad (4)$$
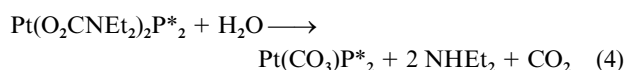
(79–94%) of Pt(CO₃)P*₂. The reaction is fast and the generally partially soluble products were recovered by filtration.

The carbonato complexes are characterized by two or three bands in the range between 1630 and 1685 cm⁻¹ (see Experimental section), where the stretching vibration of the C–O bond not involved in coordination to platinum is expected. This finding is in agreement with the literature data on bidentate carbonato complexes;[17b,f,g] the higher multiplicity with respect to what is expected on the basis of the local symmetry may be due to crystalline effects (the IR spectra were measured as Nujol mulls).

The ¹³C NMR spectrum (see Table 1) of the more soluble carbonato complex, Pt(CO₃)(PEt₃)₂, exhibits an O₃C resonance accompanied by satellites due to coupling with ¹⁹⁵Pt (60 Hz).

The bidentate nature of the carbonato ligand was confirmed by an X-ray diffraction experiment on a single crystal of Pt(CO₃)(PPh₃)₂·2CHCl₃,[17h] which showed no novel structural features with respect to other structurally established carbonato complexes of platinum(II).[17a–g]

The carbonato complexes Pt(CO₃)(PR₃)₂ (R = Ph,Et) react with MeI forming (MeO)₂CO and PtI₂(PR₃)₂. The reactions are moderately fast (12–20 h) at room temperature and can be followed by IR and NMR spectroscopies. A recent review article[18a] dealing with organic carbonates summarizes their preparation from metal carbonates. Alkylation with alkyl halides can be carried out using phase-transfer catalysts.[18b,c] Our complexes have a moderate or good solubility in organic solvents, an attribute which is presumably responsible for their

successful reaction under mild conditions in the absence of a catalyst.

The reaction of the bis(triphenylphosphino) derivative *cis*-Pt(O$_2$CNEt$_2$)$_2$(PPh$_3$)$_2$ in toluene with CO at atmospheric pressure and at room temperature afforded the carbamoyl compound *cis*-Pt[C(O)NEt$_2$]$_2$(PPh$_3$)$_2$ as the main product, see eqn. (5) . No intermediate carbonyl complexes could be

$$cis\text{-}Pt(O_2CNEt_2)_2(PPh_3)_2 + 2\,CO \longrightarrow$$
$$cis\text{-}Pt[C(O)NEt_2]_2(PPh_3)_2 + 2\,CO_2 \quad (5)$$

detected spectroscopically, although pre-coordination of carbon monoxide to platinum is assumed to occur in order to explain the observed formation of the product. The carbamoyl complex *cis*-Pt[C(O)NEt$_2$]$_2$(PPh$_3$)$_2$ is a nearly colourless solid, stable in air for some hours, sparingly soluble in toluene, soluble in chloroalkanes with slow decomposition. It is moderately stable under CO, undergoing slow reduction to platinum(0) complexes, see below.

The IR spectrum of the product of reaction (5) shows a band at 1547 cm^{-1}, attributed to the carbamoyl carbonyl stretching vibration, in agreement with literature data on other platinum(II) carbamoyl species, for example Pt(CONR$_2$)-(PPh$_3$R')$_2$ [R = Me, Et; R' = Ph].[19]

The reaction may proceed through attack at pre-coordinated CO by free amine, the latter originating from fortuitous hydrolysis, followed by protonation of the carbamato ligand to produce CO$_2$ and amine, see Scheme 1.
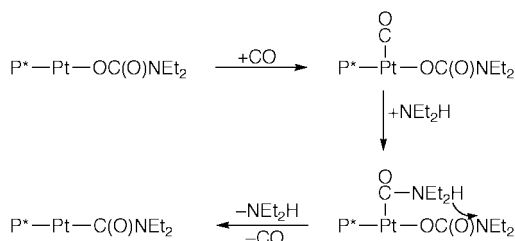
Scheme 1   P* = PPh$_3$; only two mutually *trans* ligands are shown.

The simplicity of the ^{31}P and ^{195}Pt NMR spectra, see Table 2, excludes the presence of relevant quantities of isomeric products. The ^{1}H NMR spectrum of the product of reaction (5) in CDCl$_3$ as solvent displays two triplets at δ 0.8 and 1.0 attributed to the methyl protons of the carbamoyl groups and four multiplets at δ 2.1, 2.7, 3.2, and 4.7 attributed to the methylene protons and a series of multiplets between δ 7.1 and 7.5 due to the aromatic protons. The number of resonances arising from the carbamoyl fragment suggests hindered rotation about the OC–NEt$_2$ bond, which causes the methyl and the methylene groups to be non-equivalent, as observed earlier for other platinum carbamoyl complexes.[20] Consistent with this assumption, the ^{13}C NMR spectra show two signals at δ 14.1 and 14.2, assigned to the methyl carbons and two signals at δ 38.8 and 44.0 for the methylene carbons; the latter resonances exhibit satellites due to ^{13}C–^{195}Pt coupling, see Experimental section. It is noteworthy that the signal due to *C*ONEt$_2$ in the ^{13}C spectrum appears as a doublet of doublets, owing to coupling with the ^{31}P nuclei: this pattern proves the *cis* geometry of the complex in solution. The signal is accompanied by a pair of satellites, due to coupling with the ^{195}Pt nucleus.

Platinum(II) carbamoyl complexes are reported in the literature, being prepared by one of the following routes: (a) from metal carbonyl (neutral or cationic) complexes and secondary amine;[20,21] (b) from PtCl$_2$L$_2$, CO and NHR$_2$;[19] (c) by oxidative addition of carbamoyl chloride to platinum(0) complexes.[21a]

The interest in carbamoyl complexes is largely related to their possible intermediacy in some important catalytic processes, such as the production of isocyanates or formamides or ureas from amines and CO.[22]
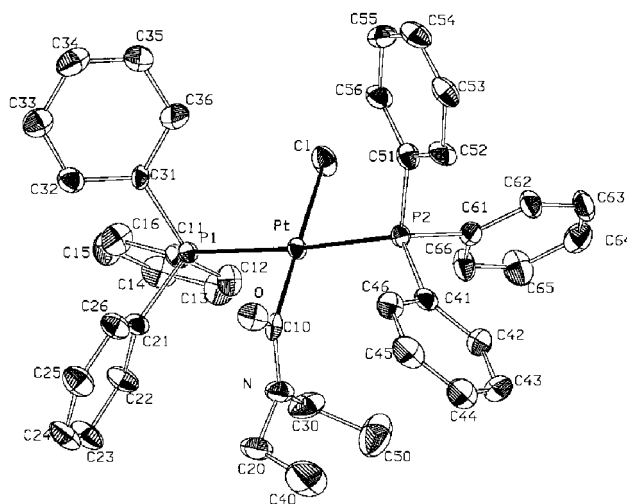
Fig. 1   The molecular structure of *trans*-PtCl[C(O)NEt$_2$](PPh$_3$)$_2$.

At variance with earlier findings,[19a] and in agreement with the results by Vasapollo *et al.*,[19b] we find that the chloride monosubstitution product can be isolated. As a matter of fact, the reaction of *cis*-PtCl$_2$(PPh$_3$)$_2$ with CO and NHEt$_2$, carried out at room temperature and at atmospheric pressure of carbon monoxide, see eqn. (6), produces *trans*-PtCl[C(O)NEt$_2$](PPh$_3$)$_2$ in relatively high yield.

$$cis\text{-}PtCl_2(PPh_3)_2 + CO + 2\,NHEt_2 \longrightarrow$$
$$\longrightarrow trans\text{-}PtCl[C(O)NEt_2](PPh_3)_2 + [NH_2Et_2]Cl \quad (6)$$
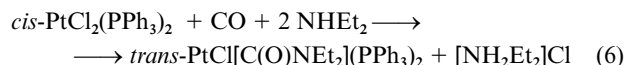
The IR and NMR spectra of *trans*-PtCl[C(O)NEt$_2$](PPh$_3$)$_2$, see Experimental section and Tables 1 and 2, exhibit the expected features: the ^{13}C and ^{1}H NMR spectra show the non-equivalence of the carbamoyl ethyl groups, while the ^{13}C resonance of *C*ONEt$_2$ at δ 168.4 is a triplet, as expected for the *trans* isomer, due to coupling with the two equivalent phosphorus nuclei.

The chloro-carbamoyl derivative reacts further and slowly with CO/NHEt$_2$ forming *cis*-Pt[C(O)NEt$_2$]$_2$(PPh$_3$)$_2$: at room temperature a 9.1 × 10^{-3} M solution of *trans*-PtCl[C(O)NEt$_2$]-(PPh$_3$)$_2$ reacts with an equimolar quantity of NHEt$_2$ in the presence of CO at atmospheric pressure, converting approximately half of the platinum complex in 20 days. The consecutive formation of *trans*-PtCl[C(O)NEt$_2$](PPh$_3$)$_2$ and *cis*-Pt[C(O)NEt$_2$]$_2$(PPh$_3$)$_2$ from *cis*-PtCl$_2$(PPh$_3$)$_2$ is consistent with a thermodynamically driven isomer formation in each step: the free ligands (NHEt$_2$, CO) in solution presumably catalyze the geometrical isomerization, as frequently observed in square-planar d^8 complexes.[23]

cis-Pt[C(O)NEt$_2$]$_2$(PPh$_3$)$_2$ decomposes slowly under CO to Pt(CO)$_2$(PPh$_3$)$_2$. Our attempts to detect the reductant and its fate led to the characterization of diethylformamide and CO$_2$ in the reaction mixture: these findings support the hypothesis that a water-assisted reduction by CO is involved. The process could proceed by coordination of carbon monoxide to platinum, followed by nucleophilic attack by water (see Scheme 2), proton transfer and loss of both CO$_2$ and HC(O)NEt$_2$.

X-Ray diffractometry of *trans*-PtCl[C(O)NEt$_2$](PPh$_3$)$_2$

The chloro-carbamoyl complex *trans*-PtCl[C(O)NEt$_2$](PPh$_3$)$_2$ was structurally characterized and the molecular structure is reported in Fig. 1.

The mononuclear complex shows the usual square-planar coordination around platinum(II), one chlorine, one carbon and two mutually *trans* phosphorus atoms constituting the chemical environment of the metal. The most relevant bond distances and angles are reported in Table 3.

Angles around platinum are about 90° and 180°, the

Table 3 Selected bond lengths (Å) and angles (°) for *trans*-PtCl[C(O)NEt$_2$](PPh$_3$)$_2$·2C$_6$H$_5$Me with e.s.d.s in parentheses

Pt–C10	2.018(8)	N–C30	1.460(12)
Pt–P1	2.311(2)	P1–C11	1.809(8)
Pt–P2	2.309(2)	P1–C21	1.840(8)
Pt–Cl	2.425(2)	P1–C31	1.841(8)
C10–O	1.204(10)	P2–C41	1.826(8)
C10–N	1.375(10)	P2–C51	1.834(8)
N–C20	1.442(12)	P2–C61	1.826(8)
C10–Pt–P1	87.7(2)	N–C30–C50	115.1(9)
C10–Pt–P2	91.3(2)	C11–P1–C21	102.9(4)
P1–Pt–P2	172.11(7)	C11–P1–C31	105.5(3)
C10–Pt–Cl	175.6(2)	C21–P1–C31	103.1(4)
P1–Pt–Cl	90.88(7)	C11–P1–Pt	115.9(3)
P2–Pt–Cl	90.68(7)	C21–P1–Pt	116.4(3)
O–C10–N	120.4(7)	C31–P1–Pt	111.7(2)
O–C10–Pt	122.3(6)	C41–P2–C51	102.2(4)
N–C10–Pt	117.3(6)	C41–P2–C61	103.1(4)
C10–N–C20	119.3(8)	C51–P2–C61	104.5(4)
C10–N–C30	122.9(7)	C41–P2–Pt	118.0(3)
C20–N–C30	117.8(8)	C51–P2–Pt	112.7(3)
N–C20–C40	116.4(9)	C61–P2–Pt	114.6(3)
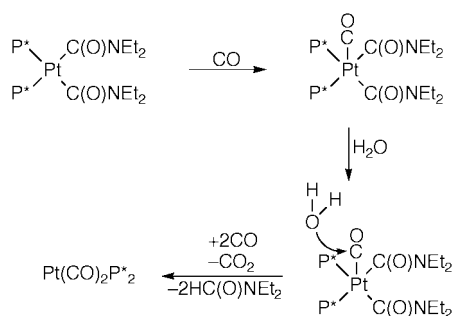
Scheme 2 P* = PPh$_3$.

maximum deviation being 7.9°. The carbamoyl group is substantially planar, as expected for a sp^2 hybridization of the carbon atom; electronic delocalization extends to the nitrogen atom, as evidenced by the N–C10 distance (1.37 Å) being shorter than the other N–C distances in the compound (1.44 and 1.46 Å) and by the geometry around the nitrogen atom characterized by bond angles close to 120°. The two Pt–P distances are equal and in the range of those usually found for a Pt–P bond with reciprocally *trans* phosphorus ligands.[24] The Pt–Cl bond is longer [2.425(2) Å] than those usually found in complexes of platinum(II) with terminal chloride (Cl$_t$) groups: by comparison of 293 cases, the average Pt–Cl$_t$ distance is 2.323(38) Å (the distances in the upper quartile being longer than 2.349 Å).[25] Nevertheless, it is similar to that observed for the Pt–Cl bond *trans* to the carbamoyl group in the anionic complex[20] *cis*-[PtCl$_2${C(O)N^{i}Pr$_2$}(CO)]$^-$, 2.404(9) Å. The Pt–C(O)NR$_2$ distance of 2.018 Å is in the range of those observed in *cis*-[PtCl$_2${C(O)N^{i}Pr$_2$}(CO)]$^-$,[20] *trans*-Pt(COCOPh)[C(O)NEt$_2$](PPh$_3$)$_2$[26] and *trans*-Pt(COCO$_2$-Me)[C(O)NEt$_2$](PPh$_3$)$_2$.[26]

Conclusions

Bis(carbamato)platinum(II) complexes having phosphines as ancillary ligands have been prepared in the course of this work: they react readily with water forming carbonato complexes. Quite often hydrolysis of metal carbamato complexes leads to oxo derivatives:[7] it is reasonable that carbonato- instead of oxo-derivatives are formed (as observed here and in the case of silver[2]) when the corresponding metal oxides are basic in nature.

The reaction of *cis*-Pt(PPh$_3$)$_2$(O$_2$CNEt$_2$)$_2$ with carbon monoxide yields the bis(carbamoyl) complex *cis*-Pt(PPh$_3$)$_2$[C(O)-NEt$_2$]$_2$: the product decomposes slowly under CO affording

Pt(PPh$_3$)$_2$(CO)$_2$, HC(O)NEt$_2$ and CO$_2$. In previous work the silver derivative Ag(O$_2$CNEt$_2$) has been reported to react with CO producing silver metal and [C(O)NEt$_2$]$_2$ and/or O[C(O)-NEt$_2$]$_2$.[2] The formation of a transient metal carbamoyl species was suggested, followed by reductive elimination of the appropriate fragments. This hypothesis is now supported by the results discussed in this paper, namely the isolation of the platinum carbamoyl derivative. The stronger M–C bond energy in the case of platinum with respect to silver may explain the different behaviour.

Experimental

All of the operations were carried out under an inert atmosphere of prepurified nitrogen. Solvents were dried by conventional methods prior to use. IR spectra were recorded with a 1725X FT-IR or 283 model Perkin-Elmer spectrophotometer in solutions or Nujol or polychlorotrifluoroethylene (PCTFE) mulls prepared under rigorous exclusion of moisture and air. ^{1}H, ^{13}C, ^{31}P and ^{195}Pt NMR spectra were recorded with a Varian Gemini 200 BB spectrometer; chemical shifts are reported in ppm *vs.* SiMe$_4$ for ^{1}H and ^{13}C, *vs.* 85% H$_3$PO$_4$ and H$_2$PtCl$_6$ in D$_2$O for ^{31}P and ^{195}Pt, respectively. The GC-MS analyses were performed with a Varian 3400 gas chromatograph with SPB-5 capillary columns (30 m × 0.22 mm) coupled to a Finnigan TSQ 700 instrument, 70 eV electronic impact. The CO$_2$ content of the carbamates was determined by gas-volumetric measurements after decomposition with CH$_3$CO$_2$H in toluene.

The following complexes were prepared according to literature procedures: Ag(O$_2$CNEt$_2$),[11] *cis*-PtCl$_2$(PPh$_3$)$_2$,[27] PtCl$_2$(DPPE)[28] and *cis*-PtCl$_2$(CO)$_2$.[29] The triethylphosphino derivative *cis*-PtCl$_2$(PEt$_3$)$_2$ was prepared from *cis*-PtCl$_2$(CO)$_2$ (1.85 g, 5.75 mmol) and PEt$_3$ (1.36 g, 11.51 mmol) in 125 cm^3 of toluene by carbonyl substitution rather than by chloride displacement[30] from [PtCl$_4$]$^{2-}$. Evolution of CO was observed during the reaction, accompanied by the formation of the compound as a colourless solid, which was collected by filtration and dried *in vacuo* (75% yield, with correct elemental analysis). IR (PCTFE, CaF$_2$ disks; Nujol, KBr disks): 2968m, 2933w, 2874w, 1466w, 1417m, 1370w, 1040m and 769m cm^{-1}. IR (Nujol, polyethylene disks): ν(PtCl)[31] 296 and 272 cm^{-1}. ^{31}P NMR (CD$_2$Cl$_2$): δ 11.1 (singlet with two satellites, J(Pt–P) = 3500 Hz). ^{195}Pt NMR (CD$_2$Cl$_2$): δ 4466 (t, J(Pt–P) = 3500 Hz).

Syntheses

***cis*-Pt(O$_2$CNEt$_2$)$_2$(PPh$_3$)$_2$ 1.** To a stirred suspension of *cis*-PtCl$_2$(PPh$_3$)$_2$(9.04 g, 11.43 mmol) in toluene (350 cm^3) Ag(O$_2$CNEt$_2$) (5.13 g, 22.90 mmol) was added at room temperature. The mixture was stirred for about 3 h (negative test for chloride in solution) and then filtered to remove the precipitate of AgCl. The brown solution was evaporated to dryness to give a light brown product, which was suspended in heptane and recovered by filtration and drying *in vacuo* (8.45 g; 78% yield). The product is extremely sensitive to moisture (Found: CO$_2$, 9.3. C$_{46}$H$_{50}$N$_2$O$_4$P$_2$Pt requires CO$_2$, 9.2%). NMR data are reported in Tables 1 and 2. IR (PCTFE, CaF$_2$ disks; Nujol, KBr disks): 3075w, 3052m, 3024w, 1600s, 1569s, 1466s, 1440s, 1408s, 1289s, 1192s, 1098s, 705s, 693s and 532s cm^{-1}.

***cis*-Pt(O$_2$CNEt$_2$)$_2$(PEt$_3$)$_2$ 2.** This compound, a colourless solid very sensitive to moisture (4.50 g, 72% yield), was synthesized similarly to compound **1** previously described, starting from *cis*-PtCl$_2$(PEt$_3$)$_2$ (4.75 g, 9.46 mmol) and Ag(O$_2$CNEt$_2$) (4.21 g, 18.79 mmol) in toluene (300 cm^3) (Found: CO$_2$, 13.0. C$_{22}$H$_{40}$N$_2$O$_4$P$_2$Pt requires CO$_2$, 13.3%). NMR data are reported in Tables 1 and 2. IR (PCTFE, CaF$_2$ disks; Nujol, KBr disks): 2968m, 2933w, 2874w, 1563w, 1494s, 1260m, 1200s, 1035s, 774s and 757s cm^{-1}.

***cis*-Pt(O$_2$CNEt$_2$)$_2$(DPPE) 3.** This compound was synthesized

from PtCl$_2$(DPPE) (1.32 g, 1.99 mmol) and Ag(O$_2$CNEt$_2$) (0.89 g, 3.97 mmol) in toluene (60 cm^3) as a colourless solid extremely sensitive to moisture (75% yield). NMR data are reported in Tables 1 and 2. IR (PCTFE, CaF$_2$ disks; Nujol, KBr disks): 3055w, 2925w, 1601s, 1572 (sh), 1407s, 1294s, 1280s, 1228m and 1206m cm^{-1}.

Pt(CO$_3$)(PPh$_3$)$_2$·C$_6$H$_5$Me, 4: by hydrolysis of Pt(O$_2$CNEt$_2$)$_2$-(PPh$_3$)$_2$. To a solution of Pt(O$_2$CNEt$_2$)$_2$(PPh$_3$)$_2$ (1.00 g, 1.05 mmol) in toluene (100 cm^3) 1.0 cm^3 of a 1.05 M solution of H$_2$O in THF (1.05 mmol of H$_2$O) was added. Immediately the colourless product precipitated out. The suspension was filtered, the solid was dried *in vacuo* and identified as Pt(CO$_3$)-(PPh$_3$)$_2$·C$_6$H$_5$Me (0.72 g, 79% yield) (Found: C, 60.2; H, 4.3. C$_{44}$H$_{38}$O$_3$P$_2$Pt requires C, 60.6; H, 4.4%). NMR data are reported in Table 2. IR (PCTFE, CaF$_2$ disks; Nujol, KBr disks): 3075w, 3052m, 3024w, 1685s, 1628m-w, 1437m, 1249m, 1098m-s, 982m, 756m, 744m and 692s cm^{-1}.

Pt(CO$_3$)(PEt$_3$)$_2$ 5. This complex was synthesised in an identical fashion to **4** by hydrolysis of Pt(O$_2$CNEt$_2$)$_2$(PEt$_3$)$_2$ (94% yield) (Found: C, 31.3; H, 6.2%. C$_{13}$H$_{30}$O$_3$P$_2$Pt requires C, 31.8; H, 6.2%). NMR data are in Tables 1 and 2. IR (PCTFE, CaF$_2$ disks; Nujol, KBr disks): 2965m, 2933w, 2874w, 1661s, 1636s, 1614m, 1412m, 1198m, 1051m and 1038m cm^{-1}.

Pt(CO$_3$)(DPPE) 6. This complex was synthesised by hydrolysis of Pt(O$_2$CNEt$_2$)$_2$(DPPE) in 92% yield (Found: C, 49.2; H, 3.6. C$_{27}$H$_{24}$O$_3$P$_2$Pt requires C, 49.6; H, 3.7%). NMR data are in Table 2. IR (PCTFE, CaF$_2$ disks; Nujol, KBr disks): 3055w, 2925w, 1662s, 1620s, 1438s, 1108m, 693m and 535s cm^{-1}.

Reactions

Pt(CO$_3$)(PPh$_3$)$_2$ with MeI. The reaction of the triphenylphosphine derivative is reported in detail, similar results being obtained with Pt(CO$_3$)(PEt$_3$)$_2$. Pt(CO$_3$)(PPh$_3$)$_2$ (0.81 g, 0.93 mmol) was dissolved in MeI (8 cm^3). The brown solution quickly turned yellow and a yellow solid precipitated out. The progress of the reaction was monitored by IR spectroscopy through the intensity of the (MeO)$_2$CO band (1754 cm^{-1}). After 20 h stirring at room temperature, the solid was filtered off, dried *in vacuo* and identified as PtI$_2$(PPh$_3$)$_2$ by IR spectroscopy (53% yield).

***cis*-Pt(O$_2$CNEt$_2$)$_2$(PPh$_3$)$_2$ with CO: synthesis of *cis*-Pt[C(O)-NEt$_2$]$_2$(PPh$_3$)$_2$ 7.** A suspension of *cis*-Pt(O$_2$CNEt$_2$)$_2$(PPh$_3$)$_2$ (2.3 g, 2.42 mmol) in toluene (50 cm^3) was stirred at room temperature under CO at atmospheric pressure. The reaction was monitored by ^{31}P NMR spectroscopy. After 18 h all of the original product had reacted and no further change was observed. The colourless carbamoyl derivative was collected by filtration and dried *in vacuo* (1.16 g, 52% yield) (Found: C, 60.5; H, 5.5; N, 2.6. C$_{46}$H$_{50}$N$_2$O$_2$P$_2$Pt requires C, 60.1; H, 5.5; N, 3.0%). IR (PCTFE, CaF$_2$ disks; Nujol, KBr disks): 3055w, 2963w, 2927w, 1547s, 1462s, 1441s, 1310m, 1239m, 1097s, 745m, 733m and 698m cm^{-1}. The NMR data are in Tables 1 and 2.

***cis*-Pt[C(O)NEt$_2$]$_2$(PPh$_3$)$_2$ under CO.** A solution of *cis*-Pt[C(O)NEt$_2$]$_2$(PPh$_3$)$_2$ (0.100 g, 0.11 mmol) in CH$_2$Cl$_2$ (5 cm^3) was stirred at room temperature under CO (p = 1 atm). The reaction was monitored by IR spectroscopy. After 24 h IR bands at 3320 (CO$_2$), 1990 and 1946 [Pt(CO)$_2$(PPh$_3$)$_2$] and 1667 cm^{-1} [HC(O)NEt$_2$] were observed. The intensities of these bands increased irregularly in the time with concomitant decrease of the bands due to *cis*-Pt[C(O)NEt$_2$]$_2$(PPh$_3$)$_2$. The reaction mixture was analyzed by GC-MS which confirmed the presence of HC(O)NEt$_2$.

Table 4 Data collection and processing parameters for *trans*-PtCl[C(O)NEt$_2$](PPh$_3$)$_2$·2C$_6$H$_5$Me

Empirical formula	C$_{55}$H$_{56}$ClNOP$_2$Pt
M	1039.49
T/K	203(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.739(3)
b/Å	12.428(5)
c/Å	17.982(3)
α/°	96.75(2)
β/°	91.82(2)
γ/°	95.62(3)
V/Å^3	2369.6(12)
Z	2
μ/mm^{-1}	3.124
Crystal size/mm	0.2 × 0.2 × 0.2
Reflections collected	11976
Independent reflections	10309 [R_{int} = 0.0257]
Reflections observed	8657
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0499, wR_2 = 0.1314

***cis*-PtCl$_2$(PPh$_3$)$_2$ with CO and NHEt$_2$: synthesis of *trans*-PtCl[C(O)NEt$_2$](PPh$_3$)$_2$ 8.** A suspension of *cis*-PtCl$_2$(PPh$_3$)$_2$ (3.20 g, 4.05 mmol) in toluene (200 cm^3) was saturated with CO at atmospheric pressure and NHEt$_2$ (5 cm^3, 48.27 mmol) was added. After 48 h stirring at room temperature, the colourless [NH$_2$Et$_2$]Cl was eliminated by filtration. The yellow solution was evaporated to dryness under reduced pressure at room temperature affording the colourless *trans*-PtCl[C(O)NEt$_2$](PPh$_3$)$_2$ (2.32 g, 67% yield) (Found: C, 57.1; H, 4.7; N, 1.3. C$_{41}$H$_{40}$-ClNOP$_2$Pt requires C, 57.6; H, 4.7; N, 1.6%). IR (PCTFE, CaF$_2$ disks; Nujol, KBr or polyethylene disks): 3058m, 2965m, 2932m, 2867w, 1574sh, 1562s, 1497m, 1482s, 1095m , 748m and 270m–s ($v_{Pt–Cl}$) cm^{-1}. The NMR data are in Tables 1 and 2.

***trans*-PtCl[C(O)NEt$_2$](PPh$_3$)$_2$ with NHEt$_2$ and CO.** A suspension of *trans*-PtCl[C(O)NEt$_2$](PPh$_3$)$_2$ (0.41 g, 0.48 mmol) in toluene (50 cm^3) was saturated with CO at atmospheric pressure and NHEt$_2$ (3.0 cm^3, 28.96 mmol) was added. After 48 h stirring at room temperature, a ^{31}P NMR spectrum of the solution showed a peak at δ 19.8 (singlet with two satellites, J(Pt–P) = 3300 Hz) due to the starting platinum complex and a peak at δ 14.6 (singlet with two satellites, J(Pt–P) = 1790 Hz) due to *cis*-Pt[C(O)NEt$_2$]$_2$(PPh$_3$)$_2$.

After 20 days, the yellow solution was evaporated to dryness under reduced pressure at room temperature and heptane was added (20 cm^3). The suspension was filtered and the yellow solid, dried *in vacuo*, was identified by ^{31}P NMR spectroscopy as a mixture of *trans*-PtCl[C(O)NEt$_2$](PPh$_3$)$_2$, *cis*-Pt[C(O)-NEt$_2$]$_2$(PPh$_3$)$_2$ and Pt(CO)$_2$(PPh$_3$)$_2$.

The same products were obtained starting from *cis*-PtCl$_2$-(PPh$_3$)$_2$, CO and NHEt$_2$ in the same solvent after a similar period of time.

Crystal structure determination of *trans*-PtCl[C(O)NEt$_2$]-(PPh$_3$)$_2$·2 C$_6$H$_5$Me

The compound was recrystallized from toluene at 0 °C. The collection of diffraction data was carried out with a CAD 4 Enraf-Nonius instrument by using Mo-Kα radiation (λ = 0.71073 Å). During data collection, three reflections were checked every hour for crystal alignment and decay. By the ω–2θ scan technique 11976 reflections were measured and corrected.[32] After averaging the intensity of the symmetry-related reflections, 10309 reflections remained, 8657 of them being considered as observed and used for the structural analysis, by using the criterion $I > 2\sigma(I)$. The crystal system being triclinic, the solution was attempted in the $P\bar{1}$ space group, which later turned out to be correct. Structure solution (Patterson method) and refinement were obtained using SHELX.[33] The details of the X-ray experiment are in Table 4.

References

1 (a) D. Belli Dell'Amico and F. Calderazzo, *N,N-Dialkylcarbamates of Transition and Non Transition Elements*, in *Advanced Syntheses and Methodologies in Inorganic Chemistry*, Bressanone, December 2–7th, 1991, *Proceedings of the Meeting*, eds. S. Daolio, E. Tondello and P. A. Vigato, 1992, p. 1; (b) D. Belli Dell'Amico, F. Calderazzo, M. Dell'Innocenti, B. Güldenpfennig, S. Ianelli, G. Pelizzi and P. Robino, *Gazz. Chim. Ital.*, 1993, **123**, 283 and refs. therein.

2 R. Alessio, D. Belli Dell'Amico, F. Calderazzo, U. Englert, A. Guarini, L. Labella and P. Strasser, *Helv. Chim. Acta*, 1998, **81**, 219.

3 L. Abis, D. Belli Dell'Amico, F. Calderazzo, R. Caminiti, F. Garbassi, S. Ianelli, G. Pelizzi, P. Robino and A. Tomei, *J. Mol. Catal. A*: *Chem*, 1996, **108**, L113.

4 L. Abis, D. Belli Dell'Amico, C. Busetto, F. Calderazzo, R. Caminiti, C. Ciofi, F. Garbassi and G. Masciarelli, *J. Mater. Chem.*, 1998, **8**, 751.

5 L. Abis, D. Belli Dell'Amico, C. Busetto, F. Calderazzo, R. Caminiti, F. Garbassi and A. Tomei, *J. Mater. Chem.*, 1998, **8**, 2855.

6 (a) D. Belli Dell'Amico, F. Calderazzo, L. Labella, G. Albanese and A. Deriu, *Gazz. Chim. Ital.*, 1988, **118**, 741; (b) A. Bacchi, D. Belli Dell'Amico, F. Calderazzo, U. Giurlani, G. Pelizzi and L. Rocchi, *Gazz. Chim. Ital.*, 1992, **122**, 429.

7 (a) D. Belli Dell'Amico, F. Calderazzo, F. Marchetti and G. Pampaloni, NATO Workshop on *Aqueous Organometallic Chemistry and Catalysis*, Debrecen, Hungary, August 28th–September 2nd, 1994, eds. I. T. Horváth and F. Joó, Kluwer, 1995, p. 199; (b) E. Agostinelli, D. Belli Dell'Amico, F. Calderazzo, D. Fiorani and G. Pelizzi, *Gazz. Chim. Ital.*, 1988, **118**, 729; (c) D. Belli Dell'Amico, F. Calderazzo, L. Labella, C. Maichle-Mössmer and J. Strähle, *J. Chem. Soc., Chem. Commun.*, 1994, 1555; (d) U. Abram, D. Belli Dell'Amico, F. Calderazzo, S. Kaskel, L. Labella, F. Marchetti, R. Rovai and J. Strähle, *Chem. Commun.*, 1997, 1941.

8 D. Belli Dell'Amico, F. Calderazzo, F. Marchetti and G. Perego, *J. Chem. Soc., Dalton Trans.*, 1983, 483.

9 D. Belli Dell'Amico, F. Calderazzo, U. Giurlani and G. Pelizzi, *Chem. Ber*, 1987, **120**, 955.

10 A. Anillo, D. Belli Dell'Amico, F. Calderazzo, M. Nardelli, G. Pelizzi and L. Rocchi, *J. Chem. Soc., Dalton Trans.*, 1991, 2845.

11 R. Alessio, D. Belli Dell'Amico, F. Calderazzo and U. Englert, *Gazz. Chim. Ital.*, 1993, **123**, 719.

12 (a) F. R. Hartley, *Nature* (*London*), 1972, **236**, 75; (b) G. Al-Takhin, G. Pilcher, J. Bickerton and A. A. Zaki, *J. Chem. Soc., Dalton Trans.*, 1983, 2657.

13 (a) R. L. Cowan and W. C. Trogler, *J. Am. Chem. Soc.*, 1989, **111**, 4750; (b) S. Park, A. L. Rheingold and D. M. Roundhill, *Organometallics*, 1991, **10**, 615.

14 (a) P. S. Pregosin, *Annu. Rep. NMR Spectrosc.*, 1986, **17**, 285; (b) P. S. Pregosin, *Coord. Chem. Rev.*, 1982, **44**, 247.

15 (a) G. K. Anderson and G. J. Lumetta, *Inorg. Chem.*, 1987, **26**, 1291.

16 R. K. Harris, *Can. J. Chem.*, 1964, **42**, 2275.

17 (a) F. Cariati, R. Mason, G. B. Robertson and R. Ugo, *Chem. Commun.*, 1967, 408; (b) P. J. Hayward, D. M. Blake, G. Wilkinson and C. J. Nyman, *J. Am. Chem. Soc.*, 1970, **92**, 5873; (c) G. B. Robertson and P. A. Tucker, *Acta Crystallog., Sect. C*, 1983, **39**, 858; (d) J. A. Davies, C. T. Eagle, A. A. Pinkerton and R. Syed, *Acta Crystallogr., Sect. C*, 1987, **43**, 1547; (e) M. R. Gregg, J. Powell and J. F. Sawyer, *Acta Crystallogr., Sect. C*, 1988, **44**, 43; (f) T. K. Miyamoto, Y. Suzuki and H. Ichida, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 3386; (g) M. A. Andrews, G. L. Gould, W. T. Klooster, K. S. Koenig and E. J. Voss, *Inorg. Chem.*, 1996, **35**, 5478; (h) Empirical formula, $C_{39}H_{32}Cl_6O_3P_2Pt$; M 1018.38, T 203(2) K, wavelength Mo-Kα ($\lambda = 0.71073$ Å), triclinic, space group $P\bar{1}$, $a = 12.31(2)$, $b = 12.89(2)$, $c = 14.930(14)$ Å, $\alpha = 106.56(6)$, $\beta = 93.57(7)°$, $\gamma = 116.98(6)°$, V 1971(4) Å^3, $Z = 2$, reflections collected 8292, independent reflections 7083 [$R_{int} = 0.0257$], final R indices [$I > 2\sigma(I)$] $R_1 = 0.0258$, w$R_2 = 0.0673$.

18 (a) A.-A. G. Shaikh and S. Sivaram, *Chem. Rev.*, 1996, **96**, 951; (b) M. Lissel and E. V. Dehmlow, *Chem. Ber.*, 1981, **114**, 1210; (c) G. Rokicki, J. Pawlicki and W. Kuran, *Polym. J.*, 1982, **14**, 839.

19 (a) W. Beck and B. Purucker, *J. Organomet. Chem.*, 1976, **112**, 361; (b) G. Vasapollo, C. F. Nobile and A. Sacco, *J. Organomet. Chem.*, 1985, **296**, 435.

20 D. Belli Dell'Amico, F. Calderazzo and G. Pelizzi, *Inorg. Chem.*, 1979, **18**, 1165.

21 (a) C. R. Green and R. J. Angelici, *Inorg. Chem.*, 1972, **11**, 2095; (b) R. J. Angelici, *Acc. Chem. Res.*, 1972, **5**, 335.

22 (a) A. Rosenthal and I. Wender, in *Organic Syntheses via Metal Carbonyls*, eds. I. Wender and P. Pino, J. Wiley, New York, 1968; (b) S. Anderson, D. J. Cook and A. F. Hill, *Organometallics*, 1997, **16**, 5595; (c) Y.-S. Lin and A. Yamamoto, *Organometallics*, 1998, **17**, 3466; (d) T.-F. Wang, C.-C. Hwu, C.-W. Tsai and Y.-S. Wen, *Organometallics*, 1998, **17**, 131.

23 F. Basolo and R. G. Pearson, in *Mechanisms of Inorganic Reactions*, J. Wiley, New York, 2nd edn., 1967; M. L. Tobe, *Inorganic Reaction Mechanisms*, Nelson, London, 1972.

24 K. W. Muir, *Mol. Struct. Diffr. Methods*, 1973, **1**, 606.

25 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.

26 T.-M. Huang, Y.-J. You, C.-S. Yang, W.-H. Tzeng, J.-T. Chen, M.-C. Cheng and Y. Wang, *Organometallics*, 1991, **10**, 1020.

27 K. A. Jensen, *Z. Anorg. Allg. Chem.*, 1936, **229**, 241.

28 A. D. Westland, *J. Chem. Soc.*, 1965, 3060.

29 F. Bagnoli, D. Belli Dell'Amico, F. Calderazzo, U. Englert, F. Marchetti, G. E. Herberich, N. Pasqualetti and S. Ramello, *J. Chem. Soc., Dalton Trans.*, 1996, 4317.

30 G. W. Parshall, *Inorg. Synth.* 1970, **12**, 27.

31 D. M. Adams, J. Chatt, J. Gerratt and A. D. Westland, *J. Chem. Soc.*, 1964, 734.

32 B. A. Frenz, Enraf-Nonius SDP-Plus Structure Determination Package, version 3.0, Delft, The Netherlands, 1985.

33 (a) G. M. Sheldrick, SHELX86, Program for the Solution of Crystal Structures, University of Göttingen, 1986; (b) G. M. Sheldrick, Program for the Refinement of Crystal Structures, University of Göttingen, 1993.

Paper 9/04868E