Inorganica Chimica Acta, 51 (1981) 15–18
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Complexes of the Type *trans*-$[PtCl_2(PR_3)(CNR')]$ and the Carbene Complex *trans*-$[PtCl_2(PR_3)\{C(NHC_6H_4Me\text{-}4)_2\}]$

JOHN R. BRIGGS, CHRISTOPHER CROCKER and BERNARD L. SHAW*
School of Chemistry, The University, Leeds LS2 9JT, U.K.

Received February 6, 1981

Treatment of chloro-bridged complexes of type $[Pt_2Cl_4(PR_3)_2]$ *with isonitriles at low temperatures gives complexes of type* trans-$[PtCl_2(PR_3)(CNR')]$, *which can be isolated. Previously only the corresponding* cis-*complexes have been described. Addition of two mole equivalents of* $CNC_6H_4\text{-}Me\text{-}4$ *to* $[Pt_2I_4(PBu^t_2Pr^n)_2]$ *in dichloromethane at* -78 *°C gives the salt* cis-$[PtI(PBu^t_2Pr^n)(CNC_6H_4Me\text{-}4)_2]I$. *Treatment of* trans-$[PtCl_2(PBu^t_2Pr^n)(CNC_6H_4Me\text{-}4)]$ *with* p-*toluidine gives the carbene complex* trans-$[PtCl_2(PBu^t_2Pr^n)\{C(NHC_6H_4Me\text{-}4)_2\}]$, *the first example of a* trans-*carbene complex of this type.*

Treatment of chloro-bridged complexes of the type $[Pt_2Cl_4(PR_3)_2]$ with neutral ligands, L, causes fission of the bridges to give mononuclear complexes of type $[PtCl_2(PR_3)L]$ which can sometimes be isolated and can be of *cis*- or of *trans*-configuration [1–3]. With L = amine *trans*-complexes are readily isolated [1–3] but with L = olefin only *cis*-complexes have hitherto been isolated: these have been studied extensively [4–8]. We have shown by NMR spectroscopy that very rapid reversible fission of a chloro-bridged complex of the type $[Pt_2Cl_4(PR_3)_2]$ by an olefin, L, such as an allylic alcohol [8], vinyl acetate [9], allyl acetate [9], ethylene, allene [10], butadiene [11] to give *trans*-$[PtCl_2(PR_3)L]$ occurs in solution

$$\begin{tikzcd}
{[Pt_2Cl_4(PR_3)_2] + 2L} \arrow[r, shift left, "\text{fast}"] \arrow[d, shift left] \arrow[d, phantom, "\text{slow}"', shift right=3] & trans\text{-}[PtCl_2(PR_3)L] \arrow[l, shift left] \\
cis\text{-}[PtCl_2(PR_3)L] \arrow[u, shift left]
\end{tikzcd}$$

and that lowering the temperature invariably increases the ratio *trans*-$[PtCl_2(PR_3)L]/[Pt_2Cl_4(PR_3)_2]$. With carbon monoxide the bridged complexes of type $[Pt_2Cl_4(PR_3)_2]$ react relatively slowly to give *cis*-$[PtCl_2(PR_3)(CO)]$ and we have shown that as with olefins, carbon monoxide at low temperatures reacts to give *trans*-$[PtCl_2(PR_3)(CO)]$ [12]. Lewis and co-workers reported in 1972 [5] that a transient species, presumably *trans*-$[PtCl_2(PR_3)(CO)]$, was formed and more recently Anderson and Cross [13–15] were able to isolate complexes of the type *trans*-$[PtCl_2(PR_3)CO]$ by working at low temperatures and by keeping down the concentration of carbon monoxide, which catalyses the isomerization of *trans*-$[PtCl_2(PR_3)(CO)]$ to *cis*-$[PtCl_2(PR_3)(CO)]$. In view of our previous work on the fission with olefins, CO and other ligands we thought that compounds of the type *trans*-$[PtCl_2(PR_3)R'NC]$ might be isolable since isonitriles, R'NC, are strongly bonding ligands to platinum. Previously bridged complexes $[Pt_2Cl_4(PR_3)_2]$ have been shown to react with isonitriles to give *cis*-complexes of type *cis*-$[PtCl_2(PR_3)(R'NC)]$ [16]. We reasoned that the isomerization *trans*-$[PtCl_2(PR_3)R'NC]$ → *cis*-$[PtCl_2(PR_3)R'NC]$ would probably be promoted by free R'NC and therefore that an excess of the dimer $[Pt_2Cl_4(PR_3)_2]$ would reduce the rate of isomerization.

In our first experiment, conducted in an NMR tube, we added 0.8 mole of p-tolyl isocyanide per Pt-atom to a solution of $[Pt_2Cl_4(PBu^t_2Pr^n)_2]$ in CH_2Cl_2/CD_2Cl_2 at -90 °C. This rapidly gave a single, new, species with ^{31}P NMR parameters $\delta P = 27.1$ ppm, $^1J(PtP) = 2898$ Hz, together with the bridged compound. A coupling constant of this magnitude is consistent with phosphine *trans* to isocyanide. This species was stable to *ca.* +8 °C but, above this temperature in the CH_2Cl_2/CD_2Cl_2 solution, another species with $\delta P = 45.5$ ppm, $^1J(PtP) = 3266$ Hz formed. This was shown to be *cis*-$[PtCl_2(PBu^t_2Pr^n)(CNC_6H_4Me\text{-}4)]$ which was synthesized in 77% yield by the general method of Chatt *et al.* [16] for compounds of this type. Microanalytical, melting point, IR and ^{31}P NMR data are given in the Tables I and II and preparative details in the Experimental. The ^{31}P NMR spectrum of this *cis*-compound at *ca.* 25 °C showed a central broad resonances with broad satellites. When the solution was cooled these resonances separated into two and, at or below

---

*Author to whom correspondence should be addressed.

TABLE I. Analytical (% Calculated Values in Parentheses) and IR (cm^{-1}) Data.

	C	H	N	Melting Point θ/°C	ν(Pt–Cl)	ν(C≡N)
cis-$[PtCl_2(PBu^t_2Pr^n)(CNC_6H_4Me\text{-}4)]$	39.95(39.8)	5.65(5.65)	2.5(2.45)	260–270[a]	290, 334	2195
trans-$[PtCl_2(PBu^t_2Pr^n)(CNMe)]$[b]	31.1(31.5)	5.75(5.7)	2.3(2.85)	164–172	340	2240
trans-$[PtCl_2(PBu^t_2Pr^n)(CNC_6H_4Me\text{-}4)]$	39.3(39.8)	5.75(5.65)	2.75(2.45)	120–122	342	2195
trans-$[PtCl_2(PEt_3)(CNBu^t)]$	28.4(28.25)	5.2(5.2)	2.95(3.0)	90–93	335	2210
trans-$[PtCl_2(PMe_3)(CNBu^t)]$	22.25(22.6)	4.1(4.25)	2.9(3.3)	145[c]	338	2230
trans-$[PtCl_2(PEt_3)(CNC_6H_4Me\text{-}4)]$	33.45(33.55)	4.45(4.4)	2.95(2.8)	78–82	350	2200
cis-$[PtI(PBu^t_2Pr^n)(CNC_6H_4Me\text{-}4)_2]I$	37.7(37.2)	4.7(4.8)	2.85(3.2)	100[a]		2190, 2170
trans-$[PtCl_2(PBu^t_2Pr^n)\{C(NHC_6H_4Me\text{-}4)_2\}]$	46.15(46.0)	6.1(6.1)	4.1(4.15)	213–216	325	

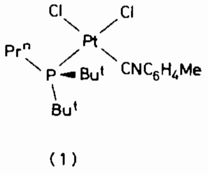
[a] With decomposition. [b] Molecular weight 490(495). [c] Decomposes without melting.

TABLE II. ^{31}P- and ^1H-NMR Parameters.

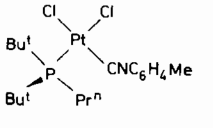
	^{31}P		^1H[b]		
	δP[a]	$^1J(PtP)$ (Hz)	δPBu^t	δCNR	$\delta ArMe$
trans-$[PtCl_2(PMe_3)(CNBu^t)]$	−22.8	2810		1.54t[c]	
trans-$[PtCl_2(PEt_3)(CNBu^t)]$	4.9	2819		1.55t[c]	
trans-$[PtCl_2(PEt_3)(CNC_6H_4Me\text{-}4)]$	6.0	2808			
trans-$[PtCl_2(PBu^t_2Pr^n)(CNC_6H_4Me\text{-}4)]$[d]	27.1[e]	2898	1.51		2.39
trans-$[PtI_2(PBu^t_2Pr^n)(CNC_6H_4Me\text{-}4)]$	49.3[e]	3098			
trans-$[PtCl_2(PBu^t_2Pr^n)(CNMe)]$	26.0	2922	1.47		
cis-$[PtCl(PBu^t_2Pr^n)(CNC_6H_4Me\text{-}4)_2]Cl$[d]	51.9	2803	1.56 1.49 [f]		2.39
cis-$[PtI(PBu^t_2Pr^n)(CNC_6H_4Me\text{-}4)_2]I$	52.1	2727			
cis-$[PtCl(PEt_3)(CNBu^t)_2]Cl$	17.9	2695			
cis-$[PtCl_2(PBu^t_2Pr^n)(CNC_6H_4Me\text{-}4)]$	45.5	3266	1.48		
trans-$[PtCl_2(PBu^t_2Pr^n)\{C(NHC_6H_4Me\text{-}4)_2\}]$	26.6	2366	1.36		2.38 2.30 [g]

[a] In ppm to high frequency of H_3PO_4 and measured in $CDCl_3$ except where stated otherwise. [b] In $CDCl_3$. [c] $^3J(^{14}NH)$ = 2.2 Hz. [d] At 0 °C. [e] In CH_2Cl_2/CD_2Cl_2. [f] At −20 °C. [g] At 20 °C, coalesced at 40 °C.

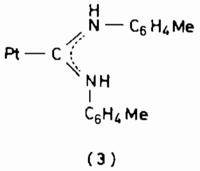
−30 °C, the resonances were sharp. The two species correspond to the two rotamers (1) and (2) corresponding to restricted rotation round the phosphorus–platinum bond because of strong interaction between the bulky t-butyl groups and the chloride or *p*-tolylisocyanide ligands. Di-tertiarybutyl-phosphine complexes frequently show rotamers due to such an interaction [17]. The ^{31}P NMR parameters for the two species are: major species δP = 46.6, $^1J(PtP)$ = 3215 Hz, minor species δP = 36.0, $^1J(PtP)$ = 3259 Hz. The *trans*-complex, *trans*-$[PtCl_2(PBu^t_2Pr^n)(CNC_6H_4Me\text{-}4)]$ was prepared by adding a deficiency (*ca.* 80%) of the p-tolyl isocyanide to a solution of $[Pt_2Cl_4(PBu^t_2Pr^n)_2]$ at *ca.* −78 °C, evaporation of the solvent at this temperature under



(1)



(2)

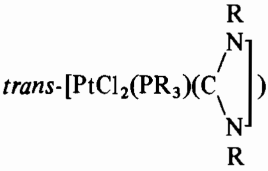


(3)

reduced pressure and recrystallization of the residue from light petroleum. We initially used [Pt$_2$Cl$_4$(PBu$^t_2$Pr^n)$_2$] as the bridged complex since we thought that the bulky phosphine, PBu$^t_2$Pr^n, might help to stabilize the *trans*-product *viz.* [PtCl$_2$(PBu$^t_2$Pr^n)(CNR)]. We then found, however, that the complexes *trans*-[PtCl$_2$(PMe$_3$)(CNBu^t)] and *trans*-[PtCl$_2$(PEt$_3$)(CNR$'$)] (R$'$ = Bu^t, *p*-CH$_3$C$_6$H$_4$) could also be prepared and isolated by the same procedure. These *trans*-complexes are all pale yellow and highly soluble in common organic solvents. They all show a single very strong peak in the far IR spectrum due to ν(Pt–Cl), at 340 cm^{-1}, characteristic of a *trans*-Cl–Pt–Cl moiety. The values of ^{1}J(PtP) for these *trans*-complexes are all *ca.* 300 Hz less than for their *cis*-isomers. In contrast, Anderson and Cross have shown that the value of ^{1}J(PtP) for *trans*-[PtCl$_2$(PR$_3$)CO] is generally greater than for the *cis*-isomer. This difference possibly reflects the stronger σ-donor and weaker π-acceptor character of isocyanides as ligands compared with carbon monoxide.

The ^{31}P NMR spectra of the complexes *trans*-[PtCl$_2$(PR$_3$)(CNBu^t)] (R = Me, Et) where both the phosphine and the isocyanide are symmetrical about the P–Pt–C axis in the complex, also show coupling to ^{14}N, ^{3}J(^{31}P–^{14}N) $\sim$ 10 Hz, so that their ^{31}P NMR spectra form a central 1:1:1 triplet flanked by satellites (due to 195-platinum). Coupling to ^{14}N is not observed with the corresponding *cis*-isomers and its presence with the *trans*-complexes reflects the higher symmetry around the P–Pt–C vector resulting in a small electric field gradient. Coupling to ^{14}N is also observed with free Bu^{t}NC [18].

As mentioned above, we found that a deuteriochloroform solution of *trans*-[PtCl$_2$(PBu$^t_2$Pr^n)(CNC$_6$H$_4$Me-4)] at 0 °C is stable but on adding one mole of 4-tolyl isocyanide, a new species, δP = 51.9 ppm, ^{1}J(PtP) = 2803 Hz formed. On attempted isolation, however, such as by evaporation of the solvent under reduced pressure at or below 0 °C and addition of light petroleum, decomposition into a mixture, consisting mainly of *cis*-[PtCl$_2$(PBu$^t_2$Pr^n)(CNC$_6$H$_4$Me-4)] and free isocyanide, occurred. We hoped that replacement of chloride by iodide might facilitate the isolation of an intermediate analogous to the above, which was probably either a five-coordinate complex, or a salt. Addition of 2.1 mole equivalents of *p*-tolyl isocyanide to [Pt$_2$I$_4$(PBu$^t_2$Pr^n)$_2$] in CH$_2$Cl$_2$ at –78 °C followed by the addition of light petroleum gives a crystalline complex which from microanalytical and conductivity data (Table I) and IR and ^{31}P NMR data (Table II) we formulate as the salt *cis*-[PtI(PBu$^t_2$Pr^n)(CNC$_6$H$_4$Me-4)$_2$]I.

It was shown by Badley, Chatt and Richards [16] that isonitrile complexes of the type *cis*-[PtCl$_2$(PR$_3$)(CNR$'$)] are attacked by alcohols or amines (nucleophilic attack) to give carbene complexes, *e.g.* a primary amine R$''$NH$_2$ gives a complex of type *cis*-[PtCl$_2$(PR$_3$){C(NHR$'$)(NHR$''$)}]. We have now treated a dichloromethane solution of *trans*-[PtCl$_2$(PBu$^t_2$Pr^n){CNC$_6$H$_4$Me-4}] with *p*-toluidine at *ca.* 20 °C. After two hours the carbene complex *trans*-[PtCl$_2$(PBu$^t_2$Pr^n){C(NHC$_6$H$_4$Me-4)$_2$}] was isolated in very good (84%) yield. Microanalytical, infrared and NMR data for this compound are in the Tables. This compound showed a single infrared absorption band at 325 vs cm^{-1} due to ν(Pt–Cl) and the low value of ^{1}J(Pt–P) of 2366 Hz (Table II) is consistent with the carbene ligand being *trans* to the phosphorus. Carbene complexes of type  $trans\text{-}[\mathrm{PtCl_2(PR_3)(C}\begin{smallmatrix}\mathrm{N{-}R}\\ \mathrm{N{-}R}\end{smallmatrix}\mathrm{)}]$ have been prepared by fission of electron rich olefins [19, 20] but ours is the first synthesis from a complex of type *trans*-[PtCl$_2$(PR$_3$)(CNR$'$)].

Carbene complexes of platinum(II) containing an amino group attached to the carbene carbon are known to exhibit restricted rotation or geometrical isomerism about the C$\overset{...}{-}$N bond [21, 22]. Our complex *trans*-[PtCl$_2$(PBu$^t_2$Pr^n){C(NHC$_6$H$_4$Me-4)$_2$}] shows a temperature dependent ^{1}H NMR spectrum but only one ^{31}P resonance, with satellites. Below 40 °C the 4-tolyl methyls are inequivalent, the two signals merging above this temperature. Since only one ^{31}P signal is observed we suggest as a tentative explanation for this behaviour that the platinum-carbene bonding is as shown in (3) and that above 40 °C rotation around the C–N bonds becomes rapid on the NMR time scale.

It was recognised by Badley *et al.* that the conversion of complexes of type *cis*-[PtCl$_2$(PR$_3$)(CNR$'$)] to carbenes is probably going *via* protonation of the nitrogen as a first step. The observation of ^{3}J(^{31}P-^{14}N) coupling in some of the *trans*-complexes gave us the opportunity to study the possible protonation of nitrogen. Addition of one mole of CF$_3$COOH to a CDCl$_3$ solution of *trans*-[PtCl$_2$(PEt$_3$)(CNBu^t)] at –60 °C removed the coupling to nitrogen giving a broad singlet in the ^{31}P NMR spectrum. When warmed to –30 °C, however, this coupling reappears. We interpret these results as indicative of reversible protonation at nitrogen at –60 °C at a rate which is at about as rapid as the NMR time scale but becomes more rapid at –30 °C. The proportion of protonated species probably decreases as temperature increases.

Experimental

^{31}P NMR spectra were recorded on a JEOL FX100 NMR spectrometer with broad band proton decoupling. ^{1}H NMR spectra were recorded at 100 MHz.

Complexes of type *trans*-$[PtCl_2(L)(CNR)]$ were all prepared and purified similarly, the preparation of *trans*-$[PtCl_2(PBu^t_2Pr^n)(CNC_6H_4Me\text{-}4)]$ is typical.

4-Tolyl isocyanide (0.017 g, 0.15 mmol) was added to a solution of $[Pt_2Cl_4(PBu^t_2Pr^n)_2]$ (0.083 g, 0.091 mmol) in dichloromethane (50 cm^3) at -78 °C. The solvent was removed under vacuum below -10 °C and the residue dissolved in light petroleum (b.p. 40–60 °C) to give the required product as yellow microcrystals (75 mg, 87%). The yields of the other four complexes of this type shown in Table I were prepared in yields of 53–71%.

cis-$[PtI(PBu^t_2Pr^n)(CNC_6H_4Me\text{-}4)_2]I$

4-Tolyl isocyanide (12 mg, 0.103 mmol) was added to a suspension of $[Pt_2I_4(PBu^t_2Pr^n)_2]$ (32 mg, 0.025 mmol) in dichloromethane (*ca.* 2 cm^3) at -78 °C. Light petroleum (b.p. 30–40 °C) was then added until the mixture just became cloudy. The mixture was then set aside at -30 °C to give the product as pale yellow needles (15 mg, 34%).

trans-$[PtCl_2(PBu^t_2Pr^n)\{C(NHC_6H_4Me\text{-}4)_2\}]$

trans-$[PtCl_2(PBu^t_2Pr^n)(CNC_6H_4Me\text{-}4)]$ (86 mg, 0.15 mmol) and 4-toluidine (65 mg, 0.61 mmol) were dissolved in dichloromethane (2 cm^3) and the resultant solution set aside at room temperature for 2 hours. Evaporation of the solvent under reduced pressure gave an oil which solidifed on addition of light petroleum (b.p. 30–40 °C). The required product formed yellow microcrystals from benzene/light petroleum (b.p. 30–40 °C). Yield 86 mg, 84%.

Acknowledgements

We thank the Science Research Council for support and Johnson Matthey Ltd. for the generous loan of platinum salts.

References

1 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 3858 (1955).

2 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 2445 (1957).

3 'Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands', Ed. C. A. McAuliffe, Macmillan Press Ltd., 1973.

4 J. Chatt, N. P. Johnson and B. L. Shaw, *J. Chem. Soc.*, 3269 (1964).

5 J. Ashley-Smith, I. Donek, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. Dalton*, 1776 (1972).

6 C. E. Holloway, C. Halley, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. (A)*, 53 (1969).

7 J. Ashley-Smith, I. Donek, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. Dalton*, 128 (1974).

8 J. R. Briggs, C. Crocker, W. S. McDonald and B. L. Shaw, *J. Chem. Soc. Dalton*, 64 (1980).

9 J. R. Briggs, C. Crocker, W. S. McDonald and B. L. Shaw, *J. Organomet. Chem., 181*, 213 (1979).

10 J. R. Briggs, C. Crocker, W. S. McDonald and B. L. Shaw, *J. Chem. Soc. Dalton*, 121 (1981).

11 J. R. Briggs, C. Crocker, W. S. McDonald and B. L. Shaw, unpublished.

12 J. R. Briggs, C. Crocker and B. L. Shaw, *Inorg. Chim. Acta, 40*, 245 (1980).

13 G. K. Anderson and R. J. Cross, *Inorg. Chim. Acta, 44*, L21 (1980).

14 G. K. Anderson and R. J. Cross, *J. Chem. Soc. Dalton*, 1988 (1980).

15 G. K. Anderson and R. J. Cross, *Chem. Soc. Reviews, 9*, 185 (1980).

16 E. M. Badley, J. Chatt and R. L. Richards, *J. Chem. Soc. (A)*, 21 (1971).

17 B. E. Mann, C. Masters, B. L. Shaw and R. E. Stainbank, *Chem. Comm.*, 1103 (1971).

18 I. D. Kuntz, P. von R. Schleyer and A. Allerhand, *J. Chem. Phys., 35*, 1533 (1961).

19 D. J. Cardin, B. Cetinkaya and M. F. Lappert, *J. Chem. Soc. Chem. Comm.*, 400 (1971).

20 D. J. Cardin, B. Cetinkaya, E. Cetinkaya and M. F. Lappert, *J. Chem. Soc. Dalton*, 514 (1973).

21 F. Bonati, G. Minghetti and G. LaMonica, *Gazz. Chim. Ital., 102*, 731 (1972).

22 E. M. Badley, B. J. L. King and R. L. Richards, *J. Organometal. Chem., 27*, C37 (1971).