Irreversible Addition of Carbon Nucleophiles to Ethylene in Cationic Platinum(II) Complexes†

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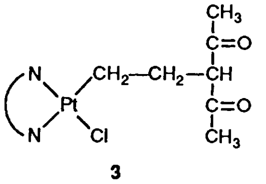
The cationic complex $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$ **1** (tmen = *N,N,N′,N′*-tetramethylethylenediamine) reacts with carbon nucleophiles [an acidic carbon substrate (HL) in the presence of a base (Na_2CO_3); HL = acetylacetone, HL^1; ethyl acetoacetate, HL^2; or diethyl malonate, HL^3] to give the corresponding addition products $[Pt(CH_2CH_2L)Cl(tmen)]$ (L = L^1, **3**; L^2, **4**; or L^3, **5**) and $[\{(tmen)ClPtCH_2CH_2\}_2(L^1 - H)]$ **6**. Compound **3** exhibits a keto–enol tautomerism. The keto tautomer is kinetically and thermodynamically favoured and in solution it represents about 90% of the equilibrium mixture; on the contrary, the enol tautomer is the favoured form in the solid. In compound **4** the carbon atom of the nucleophile which has bound to ethylene is chiral and, as a consequence, the methylene protons exhibit a diastereotopic splitting which is greater for the methylene group next to platinum than for that next to the asymmetric carbon. Treatment of compounds **3**–**6** with acids (HCl or $HClO_4$) does not reverse the carbon to carbon coupling but cleaves the platinum–carbon bond, forming the ethylated nucleophile and $[PtCl_2(tmen)]$ or $[\{PtCl(tmen)\}_2][ClO_4]_2$ depending on the acid used. The cationic complex $[Pt(\eta^2\text{-}C_2H_4)(NO_2)(tmen)]^+$ **2** reacts with carbon nucleophiles in a similar way to **1**. Treatment of the addition products with $HClO_4$ under an ethylene atmosphere gives the ethylated nucleophile and the starting complex **2**.

Nucleophilic addition to unsaturated molecules is widely investigated,[1] interest being focused on cationic complexes of olefins owing to their enhanced reactivity[2] and synthetic utility.[3] We have already reported on the cationic platinum(II) complex $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$ **1** (tmen = *N,N,N′,N′*-tetramethylethylenediamine)[4] which reacts with several nucleophiles including inorganic anions (*e.g.* NO_2^-, N_3^-, or NCO^-), hydroxide, alkoxides and carboxylates to give the corresponding addition products.[5] Under similar conditions neutral monoene platinum(II) species would have given olefin substitution rather than addition.[6]

We have now explored the reactivity of **1** and of the analogous complex **2**, in which NO_2^- has been substituted for Cl^-, towards carbon nucleophiles. Addition of stabilized carbanions to olefin complexes of platinum and palladium has already been reported for chelate dienes.[7–9] The carbon to carbon bond coupling was reversed by electrophiles and cleavage of the metal–carbon bond ought to occur under basic and/or reductive conditions. In one case addition of carbanions to monoolefinic cationic complexes of palladium(II) was reported; the corresponding addition products underwent thermolysis *via* β-hydrogen elimination upon heating to 50 °C.[10]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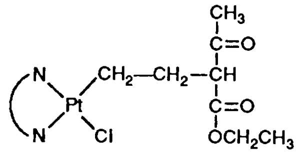
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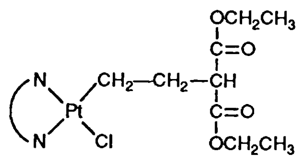
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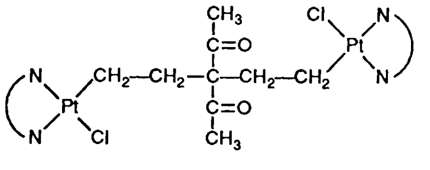
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Results and Discussion

Complex **1** reacts smoothly with carbon nucleophiles [an acidic carbon substrate (HL) in the presence of a base (Na_2CO_3) in chlorinated solvents; HL = $H_2C(COCH_3)_2$ (acetylacetone, HL^1), $H_2C(COCH_3)(CO_2CH_2CH_3)$ (ethyl acetoacetate, HL^2), or $H_2C(CO_2CH_2CH_3)_2$ (diethyl malonate, HL^3)] to give the addition compounds $[Pt(CH_2CH_2L)Cl(tmen)]$ (L = L^1, **3**; L^2, **4**; or L^3, **5**) and $[\{(tmen)ClPtCH_2CH_2\}_2(L^1 - H)]$ **6**. The reaction takes place at room temperature and does not require anhydrous conditions; it can be performed even in water although in this solvent the reaction products are contaminated by some hydroxide addition complex $[Pt(CH_2CH_2OH)Cl(tmen)]$. Under these conditions HL^1 ($pK_a \approx 9$) is the most reactive followed by HL^2 ($pK_a \approx 11$) and then by HL^3 ($pK_a \approx 13$)[11] indicating that the most acidic substrate is also the most reactive. In compound **3** the residual hydrogen atom on the nucleophilic carbon which has added to ethylene is sufficiently acidic to be replaced by a second ethylplatinum moiety to give **6**.

Treatment of compounds **3**–**6** with acids does not reverse the carbon to carbon coupling but cleaves the platinum–carbon bond yielding the ethylated nucleophile. The best results, from the point of view of recovering the organic compound, were obtained by bubbling gaseous HCl through a solution of **3**–**6** in chlorinated solvents. The platinum-containing residue separates as solid $[PtCl_2(tmen)]$ **7** while the organic component is left in solution where it remains stable also when containing ester functions.

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† *Non-SI unit employed:* atm = 101 325 Pa.

Table 1 Proton chemical shifts [δ, downfield from $Si(CH_3)_4$; J(Pt–H) in Hz in parentheses when assignable] for complexes **1**–**6** and **9**

			tmen		$PtC_\alpha H_2C_\beta H_2L$		L			
Complex	Isomer	Solvent	$N(CH_3)_2$	$>NCH_2CH_2N<$	$C_\alpha H_2$	$C_\beta H_2$	CH	CH_2	CH_3	OH
1[a]		CD_2Cl_2	3.02(35)	3.10						
			2.85(36)							
2[b]		CD_2Cl_2	3.04(40)							
			2.73(27)							
3	Keto	CD_2Cl_2	2.86(52)		1.17(88)	1.80	3.73		2.16	
			2.67(14)							
	Enol		2.87(52)		1.29(85)	2.22[c]			2.22[c]	16.65
			2.69(18)							
4		$CDCl_3$	2.92(52)	≈2.75	1.38(≈90)	1.85	3.52	4.13	2.33	
			2.89(52)	2.53	1.17(92)	1.95				
			2.71						1.19	
			2.70							
5		$CDCl_3$	2.92(51)	2.77	1.29(88)	1.93	3.35	4.13	1.23	
			2.71(13)	2.52						
6		$CDCl_3$	2.91(≈50)		1.04(88)	2.00			2.16	
			2.69							
9	Keto	CD_2Cl_2	2.77(41,17)		1.23(92)	1.84	3.68		2.15	
	Enol		2.78(17)		1.38(92)	2.13			2.17	16.67
			2.77(42)							

[a] δ 4.76 (J 60 Hz) for η^2-C_2H_4. [b] δ 4.92 (J 65 Hz) for η^2-C_2H_4. [c] The signals of $C_\beta H_2$ and CH_3 are distinguishable from their different multiplicity (triplet and singlet respectively); moreover, as is always observed, the CH_3 groups of the enol tautomer are magnetically equivalent.

Table 2 Proton chemical shifts [δ, downfield from $Si(CH_3)_4$; $CDCl_3$] of the protonated nucleophiles (HL) and of their ethylated analogues obtained by protolysis of complexes **3**–**6** and **9**

Compound	Isomer	OH	COCHCO	CH_3CO	CH_3CH_2C (CH₃)	CH_3CH_2C (CH₂)	CH_3CH_2O (CH₃)	CH_3CH_2O (CH₂)
HL^1	Keto		3.57	2.23				
	Enol	15.52	5.47	2.03				
$CH_3CH_2L^1$	Keto		3.50	2.16	0.91	1.88		
	Enol	16.30		2.11	1.05	2.21		
HL^2			3.38	2.22			1.23	4.15
$CH_3CH_2L^2$			3.33	2.24	0.97	1.91	1.30	4.20
HL^3			3.31				1.24	4.16
$CH_3CH_2L^3$			3.24		0.99	1.94	1.29	4.19
$(CH_3CH_2)_2(L^1 - H)$				2.07	0.71	1.92		

The platinum–carbon bond can also be cleaved by addition of aqueous $HClO_4$ to a chloroform solution of complexes **3**–**6**. In this case the platinum-containing residue is recovered as $[\{PtCl(tmen)\}_2][ClO_4]_2$ **8**. The reaction was performed also in the presence of ethylene (an olefin pressure of only 5 atm was used) in the hope of inhibiting the formation of **8** in favour of **1**. This, however, was not the case and **8** was always the product either because of its intrinsic thermodynamic stability or because of its low solubility in this solvent. Therefore we considered the possibility of replacing the chlorine ligand in compound **1** by another ligand having a smaller tendency to act as a bridge for platinum. Under these circumstances the formation of a species like **8** would be disfavoured. The choice fell on the nitrite anion which is a good ligand for platinum but can seldom behave as a bridging group for this metal.[12,13]

The complex $[Pt(\eta^2\text{-}C_2H_4)(NO_2)(tmen)]^+$ **2** was prepared by the reaction of **1** with excess of nitrite. The anion acts as a nucleophile towards both the ethylene and the metal centre giving chloride substitution and olefin addition and forming $[Pt(CH_2CH_2NO_2)(NO_2)(tmen)]$. Treatment of this latter species with perchloric acid affords compound **2**. It is to be noted that the pattern of protolysis is very much dependent upon the nature of the added nucleophile and in the case of inorganic anions[5b] and oxoanions[5c] only reversal of the addition reaction is observed.

Complex **2**, like **1**, is very reactive towards carbon nucleophiles and gives addition compounds similar to **3**–**6** but having a nitrite in place of the chloride ion, *e.g.* $[Pt(CH_2CH_2L^1)(NO_2)(tmen)]$ **9**. Treatment of **9** with a stoichiometric amount of aqueous $HClO_4$ led to a solution containing both the ethylated L^1 and the metallic species. Addition of ethylene (*ca.* 5 atm) caused the separation, as a white crystalline solid, of the perchlorate salt of **2** in over 70% yield. The former solution could either contain a soluble and labile dimeric complex analogous to **8** but with NO_2^- bridging groups, or, more probably, a monomeric species having a solvent molecule in the fourth co-ordination site; this point has not been fully explored at this stage.

Proton NMR and IR Data.—Relevant ^1H NMR data are reported in Tables 1 and 2. The proton resonances of the tmen ligand are slightly shifted to higher field for compounds **3**–**6** with respect to the parent cationic complex **1**. Moreover in **3**–**6** the two *N*-methyl signals have remarkably different coupling constants with the ^{195}Pt nucleus [^3J(Pt–H) ≈ 50 Hz for the lower-field signal and ≈15 Hz for the upper one]. We assigned the signal with larger coupling to the amine group *trans* to the chlorine ligand, and that with smaller coupling to the amine group *trans* to the carbon atom since this latter suffers a greater *trans* influence.[14] For compound **1** the signals of the *N*-methyl groups *trans* to Cl and to η^2-C_2H_4 both had ^3J(Pt–H) = 35 Hz. Therefore, although there is crystallographic evidence that η^2-ethylene and σ-alkyl groups cause a similar lengthening of the Pt–N bond *trans* to them,[4b,15] nevertheless their effects upon the ^3J(Pt–H) of the *trans* ligand are remarkably different.

In complex **2** the methyl groups of the tmen ligand have different couplings with the platinum nucleus (40 and 27 Hz respectively). For the addition compound **9** the ^{195}Pt coupling constant increases for the methyl groups *trans* to NO_2^- (from 27 to 41 Hz) and decreases for the methyl groups *trans* to carbon (from 40 to 17 Hz).

The resonances of the methylene protons in compounds **3**–**6** and **9** fall within 1.2–1.4 ppm downfield from $Si(CH_3)_4$ for those next to platinum (the same methylene in the addition products of nitrogen or oxygen nucleophiles occurred at slightly higher field)[5c] and within 1.8–2.2 ppm for those next to the added nucleophile. The protons of the carbanions fall in their normal range.

Compound **3** exhibits a keto–enol tautomerism of the acetylacetonate. The keto isomer has resonances at δ 3.73 and 2.16 for CH and CH_3 protons respectively, the enol isomer resonances at δ 16.65 and 2.22 for OH and CH_3 protons respectively. The rate of interconversion of the two forms is quite slow and, under appropriate experimental conditions, pure samples of the two tautomers could be obtained.[16] For instance the keto form, being kinetically favoured, is the only isomer present in the early stage of the reaction and can be separated pure from the mother-liquor. At the end of the reaction both isomers are present but the ratio (9:1) is still in favour of the keto form. The enol tautomer can be separated from a mixture of the two isomers owing to its lower solubility in water. If a mixture of the two tautomers (or even the pure keto isomer) is suspended in water and the mixture stirred for 1 d the solid material is completely converted into the pure enol tautomer while the mother-liquor contains a mixture of the two forms in the usual keto/enol ratio of 9:1. A keto–enol transformation occurs also in the solid state as shown by ^1H NMR and IR spectra of samples of compound **3** where the percentage of enol tautomer increased with increasing age. The crystal lattice stabilization of the enol tautomer is in line with its lower solubility in water.

In compound **4** the carbon atom of the nucleophile which has added to ethylene is chiral and as a consequence the co-ordination plane of platinum is no longer a plane of symmetry. This situation is clearly featured in the ^1H NMR spectra. The four methyl groups of tmen give rise to four different signals; the chemical shift difference is 0.03 and 0.01 ppm for the methyl groups *trans* to chlorine and to carbon respectively. We also noted a diastereotopic splitting of the methylene protons of ethylene which is greater for the methylene adjacent to the metal than for that adjacent to the chiral carbon (0.21 and 0.10 ppm respectively).

Some useful structural information is also gained from infrared spectra. For the addition products **3** and **9** the ν(CO) of the keto tautomer appears as a sharp intense absorption band at 1700 cm^{-1}; the same vibration in the enol isomer appears as a broad band centred at 1600 cm^{-1}. The infrared spectrum gives good evidence of the presence, in a solid sample, of only one or both tautomers.

In the nitro complexes **2** and **9** $\nu_{asym}(NO_2^-)$ and $\nu_{sym}(NO_2^-)$ are both shifted towards higher frequencies with respect to the free anion indicating that co-ordination to platinum occurs through the nitrogen atom.[12]

Conclusion

The results reported here have, once more, evidenced the great electrophilicity of olefins in cationic complexes of platinum(II). The reaction conditions are among the mildest so far reported for nucleophilic addition of carbanions to metal complexes. The addition compounds have proved to be very stable and the carbon to carbon coupling is not reversed by electrophiles such as H^+ or even Ph_3C^+. Therefore in an acidic medium the addition compounds readily undergo Pt–C bond cleavage and formation of the alkylated nucleophile. The possibility of restoring the parent cationic compound by an appropriate choice of the ancillary ligands (NO_2^-) and of the protolysis conditions ($HClO_4$) appears to be very promising for developing a catalytic cycle.[17] It is to be stressed that by this procedure an ethyl group can be selectively introduced into a carbon nucleophile while C dialkylation can be avoided and O alkylation is totally absent.

Experimental

Starting Materials.—Commercial reagent-grade chemicals, $H_2C(COCH_3)_2$, $H_2C(COCH_3)(CO_2CH_2CH_3)$ and $H_2C(CO_2CH_2CH_3)_2$ were used without further purification. *N,N,N′,N′*-Tetramethylethylenediamine was purchased from Aldrich and purified before use by distillation from potassium hydroxide. The complex $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]ClO_4$ **1** was prepared according to ref. 5*a*. Dry chlorinated solvents were obtained by distillation from calcium hydride.

Preparation of Complexes.—$[Pt(\eta^2\text{-}C_2H_4)(NO_2)(tmen)]ClO_4$ **2**. Compound **1** was suspended in water (1 mmol in 5 cm^3 of solvent) and treated with $NaNO_2$ (2.5 mmol) with stirring. The complex $[Pt(CH_2CH_2NO_2)(NO_2)(tmen)]$ separated as a white solid which was collected, dried, and then hydrolysed with a slight excess of $HClO_4$ in aqueous methanol to give **2** in 80% yield (Found: C, 19.7; H, 4.2; Cl, 7.0; N, 8.5. Calc. for $C_8H_{20}ClN_3O_6Pt$: C, 19.8; H, 4.2; Cl, 7.3; N, 8.7%).

$[Pt(CH_2CH_2L)Cl(tmen)]$ ($L = L^1$, **3**; L^2, **4**; *or* L^3, **5**). A suspension of complex **1** in dichloromethane (1 mmol in 10 cm^3) was treated with an excess of the appropriate organic reagent (HL, 3 mmol) in the presence of sodium carbonate (2–3 mmol). After stirring for several hours at room temperature (20 h in the case of L^1, 40 h in the case of L^2 and L^3) the reaction was stopped, the solution was filtered to remove the inorganic salts and taken to dryness by evaporation of the solvent under reduced pressure. The oily residue was treated with pentane and eventually with diethyl ether to give a white solid. The crude product (contaminated by unreacted **1**) was extracted with chloroform (in which **1** is not soluble), the solution was filtered and the solvent evaporated under vacuum to leave the desired compound. The yield of the isolated species was above 90% in the case of **3** and **4**, about 60% in the case of **5** (Found: C, 33.0; H, 5.8; Cl, 7.3; N, 5.9. Calc. for $C_{13}H_{27}ClN_2O_2Pt$ **3**: C, 32.9; H, 5.7; Cl, 7.5; N, 5.9. Found: C, 33.1; H, 6.0; Cl, 7.1; N, 5.6. Calc. for $C_{14}H_{29}ClN_2O_3Pt$ **4**: C, 33.4; H, 5.8; Cl, 7.0; N, 5.5. Found: C, 33.2; H, 5.9; Cl, 7.2; N, 5.2. Calc. for $C_{15}H_{31}ClN_2O_4Pt$ **5**: C, 33.7; H, 5.8; Cl, 6.6; N, 5.2%).

Complex **3** can exist in two tautomeric forms which can be isolated as pure isomers. The keto tautomer is kinetically favoured and can be obtained pure by performing the reaction according to the general procedure given above but operating at lower temperature and stopping the reaction well before it is complete (*e.g.* a reaction time of 6 h at 0 °C). If a mixture of the two tautomers (or even the pure keto isomer) is suspended in water and the mixture stirred for 1 d the solid material is completely converted into the pure enol tautomer while the mother-liquor contains a mixture of the two forms in the usual keto/enol ratio of 9:1.

$[\{(tmen)ClPtCH_2CH_2\}_2(L^1 - H)]$ **6**. This compound was obtained by following the general procedure given above but using a 2:1 molar ratio of **1** and HL^1. After stirring for 48 h at room temperature and working up of the reaction solution, a mixture of **3** and **6** in a 2:1 ratio (as evaluated from ^1H NMR data) was obtained. The compounds could be separated by column chromatography on silica gel (Found: C, 30.0; H, 5.8; Cl, 8.0; N, 6.8. Calc. for $C_{21}H_{46}Cl_2N_4O_2Pt_2$ **6**: C, 29.7; H, 5.5; Cl, 8.4; N, 6.6%).

$[Pt(CH_2CH_2L^1)(NO_2)(tmen)]$ **9**. Complexes analogous to **3**–**6** but containing a nitrite in place of a chloride ion were prepared according to the general procedure given above but starting from the cationic complex **2**. Full data are given for the complex with acetylacetonate **9**, yield 90% (Found: C, 31.8; H, 5.5; N, 8.4. Calc. for $C_{13}H_{27}N_3O_4Pt$: C, 32.2; H, 5.6; N, 8.7%).

Nucleophilic Addition in Water.—The reaction of complex **1** with HL[1] (1 mmol of each) was also carried out in water (10 cm^3) made basic with Na_2CO_3 (3 mmol). After stirring for 1 h the solution was extracted with a chlorinated solvent (CH_2Cl_2 or $CHCl_3$). The extract was dried over anhydrous Na_2SO_4, the solvent evaporated under reduced pressure, and the oily residue triturated with diethyl ether to give a white solid which comprised a mixture of complexes **3** and **6** contaminated by some hydroxide addition product.

Cleavage of Pt–Cl *Bond.*—*By* HCl. Gaseous HCl was bubbled for a few seconds through a chloroform solution of compounds **3**–**6** (0.5 mmol in 6 cm^3 of solvent). An instantaneous reaction took place. The metal-containing residue precipitated as $[PtCl_2(tmen)]$ **7** while the ethylated nucleophile stayed in solution. On performing the reaction directly in a deuteriated solvent the organic product could be identified by ^1H NMR spectroscopy of the solution after it had been left for some hours over anhydrous sodium carbonate to remove traces of acid and water.

The cleavage of complexes **3**–**6** could also be performed with aqueous HCl. The solid complex (0.5 mmol) was treated with HCl (1 cm^3 of a 2 mol dm^{-3} solution) and the mixture stirred for 2 h. The complex $[PtCl_2(tmen)]$ **7** precipitated quantitatively while the organic product could be recovered from the reaction solution after neutralization and extraction with a chlorinated solvent. In the case of **4** and **5** considerable hydrolysis of the ester functions took place.

By $HClO_4$. A chloroform solution of compounds **3**–**6** (0.25 mmol in 3–4 cm^3 of solvent) was treated with a stoichiometric amount or a slight excess (20%) of concentrated $HClO_4$ (70% in water) with stirring. A small amount of ethanol (2 cm^3) was also added to ensure miscibility of the organic and aqueous phases. In a few seconds a yellow precipitate of $[\{PtCl(tmen)\}_2][ClO_4]_2$ **8** was formed (Found: C, 16.5; H, 3.7; Cl, 15.5; N, 6.1. Calc. for $C_{12}H_{32}Cl_4N_4O_8Pt_2$: C, 16.1; H, 3.6; Cl, 15.9; N, 6.3%). The organic compound was recovered from the reaction solution by distillation of the solvent after neutralization and drying over Na_2CO_3–Na_2SO_4.

Restoration of the Starting Olefin Substrate from Compound **9**.—The acidolysis of complex **9** with $HClO_4$, according to the previous description, led to a pale green solution containing both the ethylated nucleophile and the metallic species. This solution was treated with ethylene under pressure (4–5 atm) and, in a few seconds, a white solid separated in over 70% yield. This proved to be the cationic complex **2**.

Physical Measurements.—Infrared spectra in the range 4000–400 cm^{-1} were recorded as KBr pellets, in the range 400–200 cm^{-1} as Polythene pellets, on a Perkin-Elmer 283 spectrophotometer, proton NMR spectra with Varian XL 200 and Bruker AM 300 spectrometers.

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