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Intramolecular Nucleophilic Addition of the Oxygen of a Nitro Ligand onto the *cis* Olefin in Cationic Complexes of Platinum(II)

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Among cationic complexes of platinum(II), $[Pt(olefin)(NO_2)(tmen)][ClO_4]$ (olefin = ethene **1b**, propene **2b**, *E*-but-2-ene **3b**, *Z*-but-2-ene **4b**; tmen = *N,N,N',N'*-tetramethylethylenediamine), complexes **2b** and **3b** have given evidence for the formation of an intramolecular metallacycle resulting from nucleophilic attack of one oxygen of the nitro ligand on the *cis* olefin which changes from an η^2- to σ-co-ordination mode.

The nature of the metal–olefin interaction is fully described by the formalism established by Chatt, Dewar and Duncanson in the early fifties,[1] and has been further supported by later and more detailed calculations.[2] In particular complexes of d^8 transition metals of general formula $[ML_3(olefin)]$ have a square planar arrangement of the co-ordinated ligands with the olefin lying perpendicular to the co-ordination plane. Different in-plane co-ordination of the unsaturated ligand has seldom been reported.[3,4] The difference in energy between the two possible orientations of the olefin was found to be very small and the observed preference for the upright position has been related to steric rather than electronic factors.[2]

We have synthesized some cationic olefin complexes of platinum, $[Pt(olefin)X(tmen)][ClO_4]$ (olefin = ethene **1**, propene **2**, *E*-but-2-ene **3**, *Z*-but-2-ene **4**; tmen = *N,N,N',N'*-tetramethylethylenediamine; X = Cl^- **a** or NO_2^- **b**),† and found evidence from ^1H NMR and IR data (Table 1) that in solution some of these species undergo an $\eta^2 \longrightarrow \sigma$ rearrangement resulting from nucleophilic attack of one oxygen of the nitro group on the *cis* olefin.

Characteristic features of the η^2-olefin complexes are: (*i*) ^2J(Pt–H) *ca.* 60 Hz for the olefinic protons, (*ii*) ^3J(Pt–H) close to 40 Hz for methyl substituents on the olefinic carbons, (*iii*) similar values of ^3J(Pt–H) (30–40 Hz) for the NMe_2 groups of the tmen ligand, in spite of being opposite to ligands of very different *trans* influence (either η^2 olefin or Cl^- or NO_2^-).[5,7]

In contrast complexes with σ-alkyl groups (obtained by attack of a nucleophile on compounds **1**–**4**) exhibit: (*i*) ^2J(Pt–H) and ^3J(Pt–H) of *ca.* 90 and 40 Hz, respectively, for H and Me groups on the carbon directly bound to platinum, (*ii*) negligible *J*(Pt–H) for H and Me protons on the β carbon, and (*iii*) very different ^3J(Pt–H) for the NMe_2 groups of the tmen ligand (10–15 Hz for the NMe_2 *trans* to the σ carbon and 40–50 Hz for the NMe_2 *trans* to Cl^- or NO_2^-).[5]

Table 1 Proton chemical shifts [δ, downfield from $Si(CH_3)_4$; *J*(Pt–H) in Hz, in parentheses when assignable] for $[Pt(olefin)X(tmen)]$-$[ClO_4]$ complexes

		Olefin			
Complex	tmen NMe_2	α-C*H*Me, α-CH_2	α-CH*Me*	β-C*H*Me	β-CH*Me*
1a	3.02(35)	4.76 (60)			
	2.85(36)				
1b	3.04(40)	4.92 (65)			
	2.73(27)				
2a	3.03(34)	4.88(59)[a]		5.16(70)[a–c]	1.99(40)[c]
	2.99(33)	4.63(67)[b]			
	2.94(31)				
	2.70(36)				
2b	2.95(50)	3.23(85)[d,e]		4.92[e–g]	1.59(9)[g]
	2.91(51)	2.90[d,f]			
	2.86(16)				
	2.84				
3b	*h*	4.98[i,j]	1.99(40)[j]	5.46[k]	2.06(50)[k]
	h	2.98[l,m]	1.10(40)[m]	3.89[n]	1.69[n]
4b	2.94(34)			5.47(66)[o]	1.73(42)[o]
	2.69(25)				

[a] ^3J(H–H) = 15 Hz. [b] ^3J(H–H) = 8 Hz. [c] ^3J(H–H) = 6 Hz. [d] ^2J(H–H) = 11.2 Hz. [e] ^3J(H–H) = 5.8 Hz. [f] ^3J(H–H) = 7.1 Hz. [g] ^3J(H–H) = 6.3 Hz. [h] The NMe_2 signals are in the range δ 3.1–2.6 and no assignment to the two different species has been made. [i] η^2 complex. [j] ^3J(H–H) = 5.9 Hz. [k] ^3J(H–H) = 6.2 Hz. [l] σ complex. [m] ^3J(H–H) = 7.3 Hz. [n] ^3J(H–H) = 6.4 Hz. [o] *J*(H–H) = 5.2 Hz.

The presence of an η^2 alkene is easily recognizable in all chloro complexes **1a** and **2a** and in compounds **1b** and **4b**. In contrast, the data of compound **3b** are consistent with the presence of two species in equilibrium. One species has ^1H NMR signals for the olefin and the tmen ligands which are in accord with an η^2-co-ordinated olefin (the *E*-but-2-ene is not in rapid rotation about the metal–olefin bond axis, even at room temperature, and therefore different signals for the two methyl groups and the two olefinic protons are observed).[7] The second species, which is more than 60% of the total, also exhibits two chemical shifts for the methyl groups of the olefin moiety but these occur at much higher field (δ 1.69 and 1.10), moreover the methyl at higher field shows a 40 Hz coupling with the ^{195}Pt nucleus [a likely value for ^3J(Pt–H)] while the other methyl has a negligible coupling with platinum. The two olefinic C*H*Me protons are also shifted to higher field with respect to

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† Compounds **1a** and **1b** were prepared according to ref. 5, and all other reported compounds by olefin metathesis. In a typical experiment 1 mmol of the ethylene compound was suspended in dichloromethane (5 cm^3) and treated with an excess of the exchanging olefin under stirring for 2 d at room temperature. Owing to their low solubility, the reaction products were recovered quantitatively by filtration of the mother-liquor. For **3b** and **4b** the crude reaction products contained some non-olefinic species. The raw material was treated with MeO^-,[6] and the addition product, which is highly soluble in methanol, separated by filtration and then treated with aqueous $HClO_4$ to restore the pure olefinic complex as a white solid [Found: C, 22.0; H, 4.6; N, 5.7. Calc. for $C_9H_{22}Cl_2N_2O_4Pt$ **2a**: C, 22.1; H, 4.5; N, 5.7. Found: C, 21.6; H, 4.4; N, 8.3. Calc. for $C_9H_{22}ClN_3O_6Pt$ **2b**: C, 21.7; H, 4.4; N, 8.3. Found: C, 23.1; H, 4.7; N, 8.1 (C, 23.3; H, 4.7; N, 8.3). Calc. for $C_{10}H_{24}ClN_3O_6Pt$ **3b** (**4b**): C, 23.4; H, 4.7; N, 8.2%].

the corresponding signals in the η^2 complex ($\Delta\delta$ 1.6 and 2.0 ppm, respectively); unfortunately coupling of these protons with the ^{195}Pt nucleus was not detectable because of overlapping with other signals (C$_\alpha$H) or the coupling being too small (C$_\beta$H).

These data can be rationalized by the assumption that a heterometallacycle is formed by internal nucleophilic attack of one oxygen of the nitro group on the *cis* olefin. This attack should occur at the *endo* face of the olefin,[8] and lead to only one pair of enantiomers (with the same chirality at the two former olefinic carbons as shown in Scheme 1). The chemical shift of the C$_\alpha$H proton is at lower field than the corresponding protons in acyclic platinum–alkyl complexes; the deshielding could result from the positive charge of the complex and/or the angle deformation due to ring strain.

The formation of a heterometallacycle is also supported by solution IR spectra showing a strong absorption band close to 1588 cm^{-1}. This band, which is absent for complexes **1b** and **4b**, can be associated with the N=O stretching of an nitrito alkyl group (NOOR); the other two bands at 1400 and 1340 cm^{-1} are characteristic of a conventional nitro ligand (NO$_2$).[9] Finally, the existence of an equilibrium between the two isomeric species of **3b** was proven by performing the reaction in the presence of methoxide leading to the formation of a unique addition product in quantitative yield.

A situation similar to that of **3b** can also be envisaged in compound **2b** having propene in the metal-co-ordination sphere. The olefin methylene protons resonate at δ 3.23 and 2.90 (at higher field with respect to the corresponding proton in the chloro complex **2a**) with ^2J(Pt–H) = 85 Hz which is much too large for an η^2-bound olefin. The C*H*Me proton resonates at δ 4.92 which is still appropriate for an η^2 olefin; however, its coupling with platinum ($<$ 10 Hz) is much smaller than that of the corresponding proton in compound **2a**. The coupling of the olefinic methyl group with the ^{195}Pt nucleus is less than 10 Hz compared with ^3J(Pt–H) of 40 Hz for the same methyl group in compound **2a**. The NMe$_2$ groups of the tmen ligand show two different couplings with ^{195}Pt and the difference between the two (35 Hz) is similar to that observed in the σ-alkyl complexes [Pt(σ-alkyl)X(tmen)] in which there is weaker coupling between the NMe$_2$ *trans* to the σ carbon and platinum than that *trans* to the inorganic anion.

Accordingly a structure similar to that of the more abundant isomer in compound **3b** is assigned to compound **2b**. Consistent with this conclusion is the strong absorption band at 1582 cm^{-1} characteristic of an nitrito alkyl group in the IR spectrum, while the bands at 1400 and 1340 cm^{-1}, typical of a conventional metal-co-ordinated nitro ligand, are missing. Therefore in **2b** the equilibrium between η^2 and σ species is shifted in favour of the latter in accord with Makovnikov's rule as shown in Scheme 2.

To the best of our knowledge this is an unprecedented example, in platinum chemistry, of heterometallacycle formation *via* intramolecular nucleophilic addition to a co-ordinated alkene. A similar reaction was reported by Andrews *et al.*[10] for some nitropalladium alkene complexes. In that case, however, the nucleophilic attack of the oxygen of the nitro group on the alkene (ethene or propene) *cis* to it led to transient species which reacted further, with transfer of the NO$_2$ moiety onto the olefin ligand. Only for much more complex alkenes, such as a substituted norbornene, could the heterometallacyclic complex be isolated and fully characterized by X-ray structure analysis. The NMR and IR data presented here are fully consistent with those reported by Andrews; moreover unambiguous structural information has been obtained from J(Pt–H) values.

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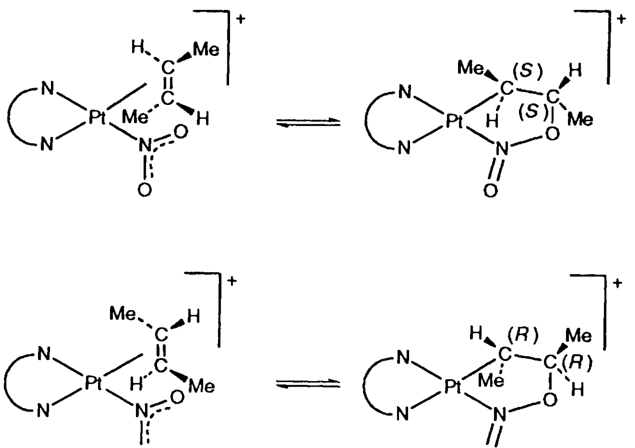
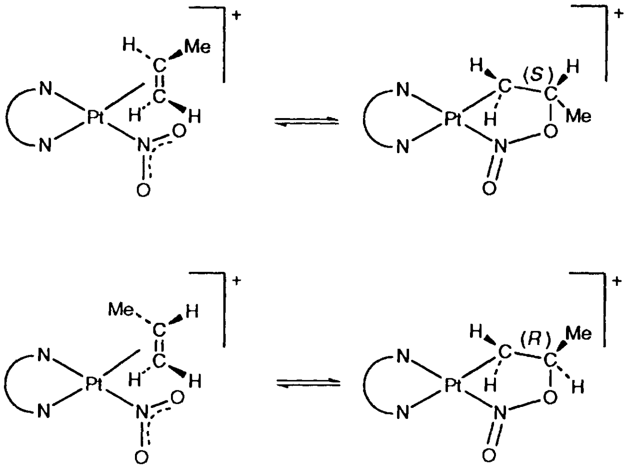


Scheme 1



Scheme 2

References

1 M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 1951, **18**, C71; M. J. S. Dewar, *Annu. Rep. Prog. Chem.*, 1951, **48**, 112; J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939; M. J. S. Dewar, R. C. Haddon, A. Komornicki and H. Rzepa, *J. Am. Chem. Soc.*, 1977, **99**, 78; M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, 1979, **101**, 783.

2 T. A. Albright, R. Hoffmann, J. C. Thibeault and D. L. Thorn, *J. Am. Chem. Soc.*, 1979, **101**, 3801 and refs. cited therein.

3 L. L. Wright, R. M. Wing, M. F. Rettig and G. R. Wiger, *J. Am. Chem. Soc.*, 1980, **102**, 5949; M. H. Rakowsky, J. C. Woolcock, L. L. Wright, D. B. Green, M. F. Rettig and R. M. Wing, *Organometallics*, 1987, **6**, 1211.

4 K. Miki, K. Yamatoya, N. K. H. Kurosawa, A. Urabe, M. Emoto, K. Tatsumi and A. Nakamura, *J. Am. Chem. Soc.*, 1988, **110**, 3191.

5 F. P. Fanizzi, F. P. Intini, L. Maresca and G. Natile, *J. Chem. Soc., Dalton Trans.*, 1992, 309.

6 F. P. Fanizzi, F. P. Intini, L. Maresca, G. Natile and F. Gasparrini, *J. Chem. Soc., Dalton Trans.*, 1990, 1019.

7 C. E. Holloway, G. Hulley, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., A*, 1969, 53.

8 R. D. Pike, W. J. Ryan, N. S. Lennhoff, J. van Epp and D. A. Sweigart, *J. Am. Chem. Soc.*, 1990, **112**, 4798.

9 M. A. Hitchmann and G. L. Rowbottom, *Coord. Chem. Rev.*, 1982, **42**, 55.

10 M. A. Andrews, T. C.-T. Chang, C.-W. F. Cheng, T. J. Emge, K. P. Kelly and T. F. Koetzle, *J. Am. Chem. Soc.*, 1984, **106**, 5913.

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