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# Coordination complexes of *C*-nitroso compounds. A $^{13}$C NMR study of some complexes of platinum with *C*-nitroso compounds

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## Abstract

Three complexes of platinum with *C*-nitroso compounds have been studied by $^{13}$C NMR spectroscopy. It has been shown that in all three cases there is a pronounced shift to higher frequency of *C*-NO and that for the two cases where this involves the t-butyl group the Pt–C coupling is evident. It is noted that this effect is stronger than for the coordination of some other ligands to platinum.

## Introduction

A small number of complexes of *C*-nitroso compounds with transition metals have been prepared and subjected to structural investigations using X-ray, IR and $^{1}$H NMR techniques. As part of a systematic study of $^{13}$C NMR spectra of *C*-nitroso compounds [1] we have extended our investigations to a number of transition metal complexes. The series of platinum complexes prepared by Mansuy et al. [2] is of particular interest in that a coordination through nitrogen is established. With the single exception of $\eta^5$-cyclopentadienyldicarbonylmanganese nitrosobenzene [3] there have been no $^{13}$C NMR studies of nitroso compound complexes for cases where there are data for the free ligand. There is virtually no published information on the $^{13}$C NMR spectra of nitrosoalkanes other than for some ring compounds containing *cis*-$N_2O_2$ groups [4] and some other *trans*-$N_2O_2$-containing molecules [6,7]. We have a wide range of additional data awaiting publication [8].

## Experimental

Dimeric 2-methyl-2-nitrosopropane was prepared by Stowell's method [9]. The compounds $[PtCl_3(RNO)]^-$ $K^+$ (R = t-Bu,Ph) and $\{PtCl_2[(CH_3)_3CNO]_2\}$ were prepared by Mansuy's method [2]. The $^{13}$C NMR spectra were recorded with a Bruker WP 200 spectrometer operating at 50.32MHz with acetone-$d_6$ as solvent for the ionic complexes and $CDCl_3$ for the covalent complexes.

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## Results

The $^{13}C$ data are listed in Table 1 and some features are illustrated in Fig. 1.

## Discussion

The crystal structure of the bis-(2-methyl-2-nitrosopropane)platinum dichloride complex established by Mansuy et al. [2] clearly demonstrates that the two nitroso ligands are separate and equivalent and N coordinated, and also that the C–N bond is unusually long at 1.56(2) Å. This contrasts with other nitrosoalkane structures; e.g., the microwave spectroscopic data for gaseous $CH_3NO$ (1.479 Å) and $CF_3NO$ (1.512 Å) [10], and the X-ray data for $C_2H_5NO \cdot CoCpPPh_3$ (1.484 Å) [11] and for the dimer of 2-methyl-2-nitrosopropane (1.533 Å) [12].

There have been a number of correlations of spectroscopic parameters of *C*-nitroso compounds with their mode of coordination to the metal, and these focus

Table 1

| Compound | *C* | *C*H$_3$ | C$_{ipso}$ | C$_o$ | C$_m$ | C$_p$ | *J*(Pt–C) (Hz) |
|---|---|---|---|---|---|---|---|
| $(t\text{-BuNO})_2$ | 76.52 | 25.11 | | | | | |
| t-BuNO | 96.4 | 23.05 | | | | | |
| $PtCl(t\text{-BuNO})_2$ | 105.59 | 27.43 | | | | | 72.3 |
| $(PtCl_3\text{-t-BuNO})^- K^+$ | 105.39 | 27.51 | | | | | 85.1 |
| $(PtCl_3PhNO)^- K^+$ | | | 172.30 | 130.15 [b] | 127.74 [b] | 136.59 | |
| PhNO [a] | | | 166.1 | 120.9 | 129.4 | 135.5 | |

[a] See ref. 1. [b] The assignment of *o*- and *m*- resonances may be reversed.

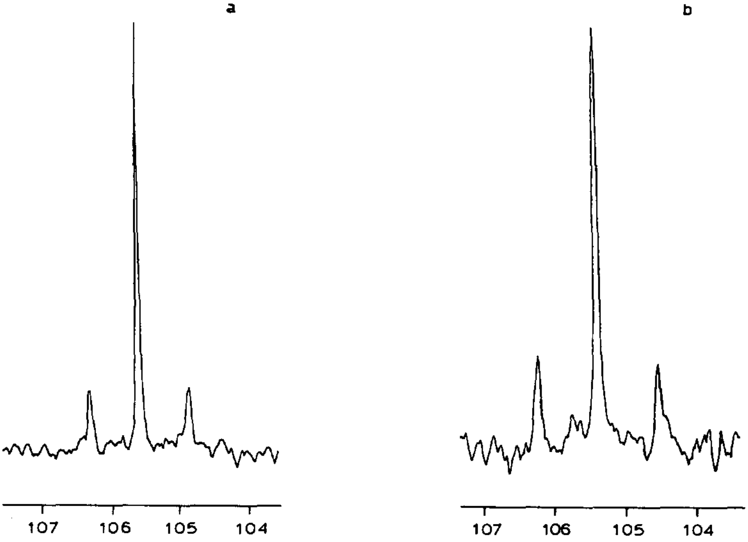

Fig. 1. $^{13}C$ NMR spectrum of (a) $\{(CH_3)_3CNO\}_2PtCl_2$ and (b) $K^+[PtCl_3(CH_3)_3CNO]^-$ illustrating $^{195}Pt$–C coupling at natural abundance. *J*(PtC) 72.3 (a) and 85.1 (b) Hz.

upon the change in $\nu$(NO), and in the $^1$H NMR spectrum of the nitroso compound. For nitrosoarenes monodentate N coordination is accompanied by a decrease in $\nu$(NO) by 10–40 cm$^{-1}$, monodentate O coordination by increase in $\nu$(NO) by 36 cm$^{-1}$, and bidentate $\pi$-NO coordination by a large decrease in $\nu$(NO) of some 470 cm$^{-1}$ [13]. Such correlations are not always straightforward, and are best aided by $^{15}$N labelling to identify the NO stretching frequency as first demonstrated by Lüttke [14]. It is not sufficient to rely solely upon infrared evidence. Certainly there is a need to have full IR spectroscopic data, and the misleading assignment of $\nu$(NO) at 1340–1350 cm$^{-1}$ due to Nakamoto and Rundle [15] should be superseded by the value of 1506 cm$^{-1}$ due to Lüttke [16] and confirmed by Strauss [17].

The simplicity of $^{13}$C NMR spectra and their interpretation results in a ready method for the study of coordination of *C*-nitroso compounds to metals. This is aided by the highly electronegative character of the NO group and the dominant character of the NO group in relation to the effect of *para*-substituents in nitrosobenzene [1], which make the assignment of *C*-NO relatively simple. The *trans*-dimeric $N_2O_2$ group is less electronegative than the monomer, and the $^{13}$C NMR spectrum is readily distinguished through temperature variation effects on the dimer/monomer equilibrium. Also there are as yet no published examples of coordination from the dimeric $N_2O_2$ group to transition metals.

It is noted that coordination through the nitrogen atom to the platinum is accompanied by a marked shift to higher frequency of the *C*-NO resonance of 9.2, 9.0 and 6.2 ppm and by shifts of the $(CH_3)_3$C and *ortho-C* in the phenyl group. It is apparent that this effect may be specific to the transition metal to which coordination takes place and/or to the stereochemistry about the metal atom rather than to the manner of coordination, i.e. through the N atom of the ligand. In the case of the 2-methyl-2-nitrosopropane ligands there is clear evidence of Pt–C coupling. Consequently we can compare the behaviour of other ligands to Pt in cases in which $^{13}$C NMR studies have been carried out. For the isonitrile complexes *trans*-$[PtCl(CNR)(PEt_3)_2]^+$ *J*(Pt–C) for the CN*C*R$^1$R$^2$R$^3$ falls in the range 15–27 Hz with shift to high frequency for alkyl carbons of 4–7 ppm [18]. The similar data for *cis*-$[PtCl_2(CNR)PEt_3]$ are 18–27 Hz and 4–5 ppm [18]. The alkyl R group in $[NPr^n_4]$ $[PtCl_2C(CO)]$ has *J*(Pt–C) in the 4–14 Hz range for the first C atom in the alkyl group after the immediately attached C [19]. In the series $(p\text{-}XC_5H_4N \rightarrow Pt(Cl)_2 \leftarrow L$ when L = t-BuC≡C-t-Bu *J*(Pt–C) 15.7 Hz for the central C of the t-Bu group and for L = PhCH=CH$_2$ *J*(Pt–C) 36.4 Hz for the *ipso*-C of the phenyl group [20]. The origins of this coupling are not commented upon in the papers concerned, but it suggests that PtC coupling is a general phenomenon for the C atom attached to the atom of the group through which coordination occurs. The *J*(Pt–C) values for the two t-butyl compounds which we have investigated suggest a stronger coupling (72.3 and 85.1 Hz).

Further extensive studies of the use of $^{13}$C NMR in assisting the establishment of the coordination mode of *C*-nitroso compounds to transition metals are in progress [21].

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