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Multinuclear NMR Studies on Rhodium(II) Acetate–Trimethylphosphite Adducts

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Since their discovery in 1960 [1], binuclear metal–metal bonded rhodium(II) carboxylates possessing the now familiar 'lantern' structure have aroused keen interest. Structure, bonding, adduct formation and more recently, anti-tumour activity [2] have all been intensively studied using a variety of physical techniques including photoelectron, electronic and vibrational spectroscopy, X-ray crystallography and magnetic measurements. However, very little NMR work has been reported on systems of this type.

We now report preliminary results from a multinuclear variable-temperature NMR study on trimethylphosphite adducts of rhodium(II) acetate, which clearly demonstrate the value of this technique in the study of rhodium(II) carboxylate systems.

The NMR spectra (^1H, ^{13}C, ^{31}P and ^{103}Rh) of '$[Rh_2(O_2CCH_3)_4\{P(OCH_3)_3\}_2]$' in CD_2Cl_2 solution can be interpreted in terms of the mono- and bis-adducts (I) and (II) respectively, free trimethylphosphite and traces of trimethylphosphate. The last species apparently forming by aerobic oxidation of free phosphite.

At ambient temperature (298 K) a dynamic equilibrium involving rapid exchange of dissociated and bound trimethylphosphite ligands is clearly occurring, signals are broad, except for $^{13}C\{^1H\}$, and there is no visible evidence of internuclear couplings. Data recorded (all in ppm) are as follows: ^1H $\delta_{C\mathit{H}_3CO_2}$ 1.83(s), $\delta_{P(OC\mathit{H}_3)_3}$ 3.89(s); ^{13}C, $\delta_{\mathit{C}H_3CO_2}$ 24.13(s), $\delta_{CH_3\mathit{C}O_2}$ 193.12(s), $\delta_{P(O\mathit{C}H_3)_3}$ 51.28(s); ^{31}P, $\delta_{\mathit{P}(OCH_3)_3}$ 91.9(s)*.

On cooling the solutions to 213 K freezing out of the free and bound trimethylphosphite exchange process leads to the appearance of sharp signals attributable to mono- and bis-adducts, (I) and (II) respectively, with well defined internuclear couplings.

The low temperature ^1H NMR spectrum comprises a singlet at 1.92 ppm $C\mathit{H}_3CO_2]$ and a doublet at 3.92 ppm, $^3J(PH)$ = 11.0 Hz $[P(OC\mathit{H}_3)_3]$ attributable to the mono-adduct (I), a singlet at 1.87 ppm $[C\mathit{H}_3CO_2]$ and a virtual coupling triplet at 3.88 ppm, N = 11.0 Hz $[P(OC\mathit{H}_3)_3]$ assigned to the bis-adduct (II), and a doublet at 3.78 ppm $^3J(PH)$ = 11.0 Hz arising from traces of free trimethylphosphate. On addition of excess trimethylphosphite (*ca.* 4 moles per mole of dimer) the signals due to the mono-adduct disappear and a new doublet pattern attributable to excess free phosphite is observed [δ 3.51 ppm, $^3J(PH)$ = 10.3 Hz].

The low temperature $^{13}C\{^1H\}$ NMR pattern is also consistent with the presence of mono- and bis-adducts. The mono-adduct (I) displays ^{13}C resonances at 23.97 ppm(s) $[\mathit{C}H_3CO_2]$, 191.60 ppm(s) $[CH_3\mathit{C}O_2]$ and 51.59 ppm(s) $[P(O\mathit{C}H_3)_3]$. Resonances at 24.20 ppm(s) $[\mathit{C}H_3CO_2]$, 193.56 ppm(t) $[CH_3\mathit{C}O_2]$ and 50.74 ppm(s) $[P(O\mathit{C}H_3)_3]$ are assigned to the bis-adduct (II). The small triplet splitting (~8.8 Hz) observed for the $CH_3\mathit{C}O_2$ carbon resonance of the bis-adduct is attributable to the coupling $[^3J(^{13}C, ^{31}P)]$. There is no visible evidence of internuclear coupling in the signal due to the $[CH_3\mathit{C}O_2]$ ^{13}C nuclei of the mono-adduct. The apparent absence of a coupling between carbon (^{13}C) and phosphorus nuclei of the trimethylphosphite ligands is tentatively attributed to the algebraic cancellation of $[^2J(^{13}C, ^{31}P)]$ and $[^5J(^{13}C, ^{31}P)]$ [3].

The $^{31}P\{^1H\}$ spectra of the product '$[Rh_2(O_2CCH_3)_4\{P(OCH_3)_3\}_2]$' obtained at 213 K consists of the X portion of an AMX pattern** attributable to the mono-adduct and the XX′ part of an AA′XX′ pattern due to the bis-adduct [A,A′,M = ^{103}Rh; X,X′ = ^{31}P]. Data obtained by the first order analysis of the X portion of the AMX pattern, and by iterative computer analysis (PANIC 80 programme [4]) of the XX′ portion of the AA′XX′ pattern are given in Table I.

Finally the low temperature ^{103}Rh spectrum of the bis adduct (II) – the AA′ part of the AA′XX′ spectrum – showed a broad but well-defined virtual coupling triplet pattern $\delta(^{103}Rh)$ 6694 ppm (N = 137.3 Hz) (Fig. 1). The ^{103}Rh signal for the mono-adduct could not be resolved.

Changes in the nature of the carboxylate do not significantly alter $^1J(^{31}P, ^{103}Rh)$, $^2J(^{31}P, ^{103}Rh)$,

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* ^1H spectra were referenced to int. TMS and were recorded at 250 MHz. ^{13}C spectra were referenced to int. TMS and were recorded at 22.63 MHz. ^{31}P spectra were referenced to ext. H_3PO_4 and were recorded at 36.44 and 162 MHz. The ^{103}Rh spectrum was recorded at 12.6 MHz. All spectra were recorded with positive frequency to low field of reference. s = singlet, d = doublet, t = triplet.

** ^{31}P NMR spectra taken at 36.44 and 162 MHz show identical rhodium–phosphorus coupling constants and thereby confirm that the spin system under examination is AMX rather than ABX.

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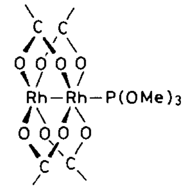
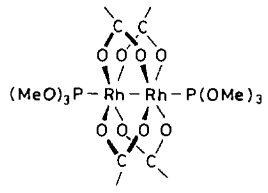
TABLE I. Coupling Constants and Chemical Shifts Calculated for Mono- and Bis-adducts (I) and (II).

(I) (mono-adduct)[a]		
$^1J(^{31}P, ^{103}Rh)$	151.4 Hz	
$^2J(^{31}P, ^{103}Rh)$	43.9 Hz	
δ_P	36.7 ppm	
II (bis-adduct)[b]		
$^1J(^{31}P, ^{103}Rh)$	134.1 Hz	
$^2J(^{31}P, ^{103}Rh)$	−1.5 Hz	
$^3J(^{31}P, ^{31}P)$	853.7 Hz	
$^1J(^{103}Rh, ^{103}Rh)$	7.9 Hz	
δ_P	93.5 ppm	
δ_{Rh}	6694 ppm	

[a] Signs of J are unknown. [b] Signs of J are relative.

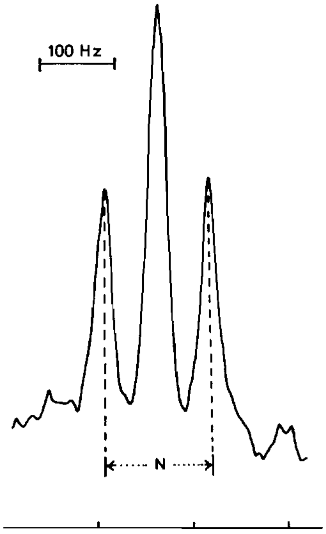


Fig. 1. ^{103}Rh NMR spectrum (12.6 MHz) of $Rh_2(O_2CCH_3)_4\{P(OCH_3)_3\}_2$.

$^1J(^{103}Rh, ^{103}Rh)$ or $^3J(^{31}P, ^{31}P)$. We have assumed that the second axial coordination site on the mono-adduct is vacant. However, the presence of coordinated solvent or water cannot be excluded.

These preliminary results clearly demonstrate the potential value of nmr measurements in structural, thermodynamic and kinetic studies of rhodium(II) carboxylate complexes. Some of these aspects will be explored in future publications.

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