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NMR STUDIES OF FLUXIONAL RHENIUM CARBONYL COMPLEXES OF 2,6-DIACETYLPYRIDINE (DAP), *fac*-[$ReX(CO)_3(DAP)$]*

KEITH G. ORRELL, ANTHONY G. OSBORNE,† VLADIMIR ŠIK and MATEUS WEBBA DA SILVA

Department of Chemistry, The University of Exeter, Exeter, EX4 4QD, U.K.

Abstract—2,6-Diacetylpyridine (DAP) reacted with pentacarbonylhalogeno rhenium(I) complexes under mild conditions to form stable octahedral complexes of the type *fac*-[$ReX(CO)_3(DAP)$] (X = Cl, Br or I) in which the DAP acts as a bidentate chelate ligand. In solution these complexes are fluxional with DAP oscillating between equivalent bidentate bonding modes by a twist mechanism involving the breaking/making of two Re—O bonds. Rates and activation energies of these fluxions have been investigated by NMR methods. 2-Acetylpyridine (AP) reacts with bromopentacarbonylrhenium(I) to form the non-fluxional chelate complex *fac*-[$ReBr(CO)_3(AP)$].

In coordination chemistry an important topic is the design and study of ligands and their influence on the structures and reactivity of the resulting metal complexes. We have studied[1] some metal complexes of potentially terdentate ligands wherein the ligands are acting in a bidentate chelate mode. Initially our interest was with planar N_3 ligands such as 2,2′ : 6′,2″-terpyridine[1] (terpy) and 2,6-bis(pyrazol-1-yl)pyridine[2] (bppy) in complexes exemplified by *fac*-[$PtXMe_3$(terpy)] and *fac*-[$ReX(CO)_3$(bppy)] (X = Cl, Br or I). In these kinetically inert octahedral complexes the N_3 ligand is forced to act in a bidentate chelate mode. Detailed NMR studies of this type of complex have demonstrated that, in solution, the complexes are fluxional and that the molecular motion involves the three donor nitrogen atoms of the ligand becoming involved with the metal via a tick–tock twist of the metal moiety through a N–metal–N angle of the octahedral centre.

We are now investigating the generality of the 1,4-metallotropic shift in other potentially terdentate ligands but which involve donor atoms other than nitrogen. Ligands that involve a group V and a group VI atom form a strong and a less strong bond, respectively, to the metal. Ligands of this type have recently been of considerable interest[3] because of the potential for increased catalytic activity of a metal centre when coordinated to a hemi-labile ligand. We now report our results on the complexes formed between [$ReX(CO)_5$] (X = Cl, Br or I) and 2,6-diacetylpyridine (DAP) and on the complex with 2-acetylpyridine (AP), *fac*-[$ReBr(CO)_3$(AP)]. As far as we can ascertain the only previous report[4] of 2,6-diacetylpyridine as a ligand is for an incompletely characterized complex of platinum(IV).

EXPERIMENTAL

Materials

The compounds [$ReX(CO)_5$] (X = Cl, Br or I) were prepared by previous methods.[5,6] 2-Acetylpyridine (AP) and 2,6-diacetylpyridine (DAP) were purchased from Aldrich.

Synthesis of the complexes

All preparations were carried out using standard Schlenk techniques[7] under purified nitrogen using freshly distilled, dried and degassed solvents.

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* Dedicated to Eddie Abel, a greatly valued friend, collaborator and colleague.

† Author to whom correspondence should be addressed.

The complexes $[ReX(CO)_3(DAP)]$ (X = Cl, Br or I) and $[ReBr(CO)_3(AP)]$ were all prepared in a similar manner. The details for $[ReBr(CO)_3(DAP)]$ are given below. The synthetic and analytical data for the four complexes are given in Table 1.

Bromotricarbonyl(2,6-*diacetylpyridine*)*rhenium*(I)

The complex $[ReBr(CO)_5]$ (0.1 g, 0.25 mmol) and DAP (0.045 g, 0.027 mmol) were dissolved in benzene (10 cm^3) with stirring and gentle warming to produce a colourless solution. This was heated under reflux for 3 h and then light petroleum (b. pt 40–60°C, 10 cm^3) was added and the solution allowed to cool. The product precipitated as a carmine red solid. The solid was removed by filtration, then washed with diethyl ether (2×15 cm^3) and dried under vacuum; yield 0.108 g (86%).

Physical methods

Solution-state ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM250 and ACF300 spectrometers operating at 250.13 and 300.13 MHz for ^{1}H and 62.90 and 75.47 MHz for ^{13}C, respectively. Spectra were recorded of $CDCl_3$ or $CDCl_2 \cdot CDCl_2$ solutions on the complexes, with $SiMe_4$ as an internal standard. Standard B-VT100 variable-temperature units were used to control the probe temperatures. Temperatures, based on calibration against a Comark digital thermometer, are considered accurate to ± 1°C. Kinetic data were derived from band-shape analysis of ^{1}H NMR spectra using the authors' version of the standard DNMR program.[8] Solid-state ^{13}C CP-MAS NMR spectra were recorded on a Varian VXR 300 spectrometer operating at 75.43 MHz, at the University of Durham Industrial Research Laboratories. Operating conditions were acquisition time 40.5 ms, relaxation delay 60.0 s and contact time 7.0 ms.

IR spectra of $CHCl_3$ solutions of the complexes were recorded on a Perkin–Elmer 881 spectrometer, calibrated from the line of polystyrene at 1602 cm^{-1}.

Elemental analyses were carried out by Butterworth Laboratories, Teddington, Middlesex, London.

RESULTS AND DISCUSSION

High yields of the complexes $[ReX(CO)_3(DAP)]$ (X = Cl, Br or I) and $[ReBr(CO)_3(AP)]$ as air-stable red crystalline solids were obtained following the above method. In $CHCl_3$ solution the complexes showed three strong carbonyl stretching bands in the IR region (Table 1), which is indicative of a *fac* stereochemistry for the complexes, and hence for AP and DAP acting as bidentate chelate ligands. This was confirmed by solution and solid-state NMR (see later).

Static NMR studies

$[ReBr(CO)_3(AP)]$. The ^{1}H chemical shifts (δ) for AP, the complex, and the coordination shifts $\Delta\delta$ are recorded in Table 2. H,H spin–spin coupling constants for the ligand and its complex are also included. It is notable that the coordination shifts are all positive with the 6-position hydrogen (H_E) having the largest magnitude. This is not surprising as this hydrogen is closest to the site of N coordination.

Table 1. Synthetic and analytical data for the complexes $[ReX(CO)_3(DAP)]$ (X = Cl, Br or I) and $[ReBr(CO)_3(AP)]$

Complex	Reaction time (h)	M.pt. (°C)[a]	Yield (%)[b]	ν_{CO} (cm^{-1})[c]			Analysis (%)[d]		
							C	H	N
$[ReCl(CO)_3(DAP)]$	3	158–160	84	2037vs	1938s	1918s	26.5	1.5	2.4
							(26.9)[e]	(1.5)[e]	(2.3)[e]
$[ReBr(CO)_3(DAP)]$	3	197–199	86	2037vs	1940s	1918s	28.1	1.8	2.7
							(27.8)	(1.7)	(2.6)
$[ReI(CO)_3(DAP)]$	4	211–213	81	2036vs	1941s	1923s	25.7	1.6	2.5
							(25.3)	(1.5)	(2.3)
$[ReBr(CO)_3(AP)]$	3	249–251	95	2034vs	1936s	1907s	25.7	1.4	2.9
							(25.5)	(1.5)	(3.0)

[a] With decomposition.

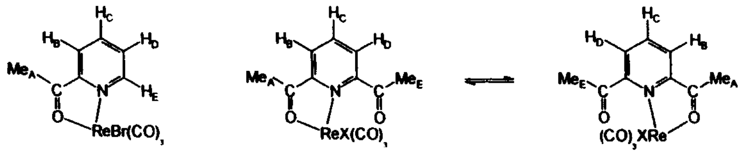
[b] Relative to $[ReX(CO)_5]$.

[c] Recorded in $CHCl_3$ solution; v = very, s = strong.

[d] Calculated values in parentheses.

[e] Figures allow for incluson of solvent of crystallization, i.e. $[ReCl(CO)_3(DAP)] \cdot CHCl_3$.

Table 2. ^{1}H and ^{13}C NMR data[a] for AP, DAP and their rhenium(I) complexes



Compound	Solvent coordination shift	Temperature (°C)	Nucleus	δ_A	δ_B	δ_C	δ_D	δ_E	J_{BC}	J_{BD}	J_{BE}	J_{CD}	J_{CE}	J_{DE}
AP	$CDCl_3$	30	^{1}H	2.63	7.94	7.74	7.38	8.58	7.9	1.3	1.0	7.6	1.6	5.0
[ReBr(CO)$_3$(AP)]	$CDCl_3$	30	^{1}H	3.00	8.35	8.22	7.81	9.15	7.7	1.4	0.7	7.7	1.4	5.5
	$\Delta\delta$[b]			0.37	0.41	0.48	0.43	0.57						
DAP	$CDCl_3$	30	^{1}H	2.77	8.19	7.97	8.19	2.77	7.8	[c]	—	7.8	—	—
[ReCl(CO)$_3$(DAP)]	$CDCl_3$	−40	^{1}H	3.09	8.45	8.41	7.86	2.88	7.8	1.6	—	7.6	—	—
	$\Delta\delta$[d]			0.32	0.26	0.44	−0.33	0.11						
[ReBr(CO)$_3$(DAP)]	$CDCl_3$	−20	^{1}H	3.07	8.46	8.37	7.83	2.87	7.8	1.4	—	7.7	—	—
	$\Delta\delta$[d]			0.30	0.27	0.40	−0.36	0.10						
	$CDCl_3$	65	^{1}H	2.93	8.20	8.28	8.20	2.93						
	$CDCl_3$	−20	^{13}C[e]	31.52	141.48	130.23	127.41	27.37						
	Solid	−30	^{13}C[f]	30.87	147.19	133.49	126.50	27.86						
[ReI(CO)$_3$(DAP)]	$CDCl_3$	−20	^{1}H	3.03	8.48	8.36	7.81	2.89	7.8	1.0	—	7.7	—	—
	$\Delta\delta$[d]			0.26	0.29	0.39	−0.38	0.12						

[a] Chemical shifts relative to $SiMe_4$ $\delta = 0$; scalar couplings J_{ij} in Hz.

[b] Coordination shifts relative to AP.

[c] Unknown since H_B and H_D are isochronous.

[d] Coordination shifts relative to DAP.

[e] Additional shifts at $\delta = 211.00$, 161.11, 150.89, 199.43, 196.12, 194.74 and 186.45.

[f] Additional shifts at $\delta = 213.83$, 160.98, 150.64 and 199.69. Re–carbonyl signals not detected.

[ReX(CO)$_3$(DAP)]. The ^{1}H chemical shifts (δ) and coordination shifts ($\Delta\delta$) are recorded in Table 2 for all three complexes (X = Cl, Br or I). In all cases the spectra consist of multiplets arising from the three non-equivalent protons of the pyridine ring plus singlets for the two methyl groups. This was clearly associated with the DAP acting in a bidentate chelate mode of bonding to rhenium. In all cases there are significant high-frequency coordination shifts at the A, B and C positions, $\Delta\delta_A \approx 0.30$, $\Delta\delta_B \approx 0.27$ and $\Delta\delta_C \approx 0.42$, smaller coordination shifts in the same direction at the E position, $\Delta\delta_E = 0.11$, and significant low-frequency coordination shifts at position D, $\Delta\delta_D \approx -0.35$. These low-frequency shifts are clearly the result of the preferred conformation of the acetyl groups, relative to the pyridyl ring, changing on metal coordination. In the free DAP the preferred conformation is most likely that when the carbonyl function is *trans* to the pyridyl N atom [cf. the *trans*, *trans* conformations of 2,2′;6′2″-terpyridine and 2,6-bis(pyrazol-1-yl)pyridine[9]]. Thus, the D-position hydrogen will be in a deshielding zone of the carbonyl moiety. For coordination to occur the carbonyl function must adopt a *cis* orientation with respect to the pyridyl nitrogen. This will lead to a relative shielding of the D position hydrogen and therefore a significant negative coordination shift.

Dynamic ^{1}H *NMR studies*

[ReX(CO)$_3$(DAP)]. At temperatures of *ca* −30°C the three complexes (X = Cl, Br or I) gave similar ^{1}H NMR spectra that were consistent with a non-fluxional bidentate chelate mode of bonding for the DAP ligand. On raising the temperature of the NMR solutions to ambient temperatures all spectral lines broadened with the exception of the H_C signal. A further increase in temperature resulted in pairs of lines eventually coalescing and then sharpening according to the exchange schemes $A \rightleftharpoons E$ and $BCD \rightleftharpoons DCB$ (Table 2). These spectral changes clearly arise from a fluxional process involving 1,4 shifts of the pair of Re—O bonds according to the pair of structures shown in Table 2. The fact that the 4-position pyridine proton is totally unaffected by this fluxion was also a characteristic of the dynamic NMR studies of other potentially terdentate ligands derived from 2,6 disubstituted pyridines.[1,2] Accompanying these spectral changes there is also evidence for some decomposition occurring, namely the dissociation of the DAP ligand from the metal complex.

Rates for the fluxional process in the three complexes were deduced by band-shape analysis of the signals of the methyl groups, Fig. 1. The activation parameters that were derived from the "best-fit" rate data are given in Table 3. $\Delta G^\ddagger$ values for the fluxion are in the range 59.4–61.5 kJ mol^{-1} and are essentially independent of halogen. The $\Delta G^\ddagger$ values for the present complexes, for related N_3 ligands and for a SNS ligand complexed to the ReX(CO)$_3$ moiety are collected in Table 4.

The independence of $\Delta G^\ddagger$ values from the halogen is probably a consequence of the small steric requirement of the acetyl group and hence a reduced likelihood of any interaction of the pendant acetyl group with the halogen. This result is consistent with our studies[2,10] of rhenium(I) complexes involving 2,6-disubstituted pyridines. Substituents of relatively small steric requirements such as pyrazole or 4-methylpyrazole exhibited $\Delta G^\ddagger$ values that are essentially independent of halogen, whereas ligands containing sterically more demanding substituents showed a slight halogen dependence in the order I > Br > Cl.

The $\Delta G^\ddagger$ values for the DAP complexes are much smaller than the values for the sulphur-containing ligand[11] and are intermediate in the range of values found for the various pyrazole ligands.[10,12] As was discussed in our previous work,[2] it is probable that electronic and geometric factors are making a contribution to the energy by influencing the formation of the quasi-terdentate form of the ligand in the transition state (see below).

In our studies of this type of 1,4-metallotropic shift in complexes of rhenium(I) and platinum(IV) which involved N_3 ligands we have demonstrated[1] that the mechanism for the fluxion involves a twist mechanism via a seven-coordinated metal intermediate. This mechanism was confirmed by the observation of the exchange of the two equatorial groups which is a necessary consequence of the mechanism. In the present work the ^{13}C spectrum (carbonyl region) of [ReI(CO)$_3$(DAP)] in $CDCl_2 \cdot CDCl_2$ was recorded at −20, 0 and 20°C (Fig. 2). The spectra show clear evidence of the exchange broadening of two of the metal carbonyl signals, presumably the equatorial pair, and of the two acetyl carbonyl signals, hence giving a definite confirmation that the mechanism is again proceeding via the "tick–tock" twist mechanism, with the making/breaking of two Re—O bonds (Fig. 3).

^{13}C *NMR studies*

^{13}C NMR spectra of [ReBr(CO)$_3$(DAP)] both in the solid state and in $CDCl_3$ solution were recorded and shift data included in Table 2. Assignments of the pyridyl carbon signals is slightly uncertain and values for the solid and solution states are sig-

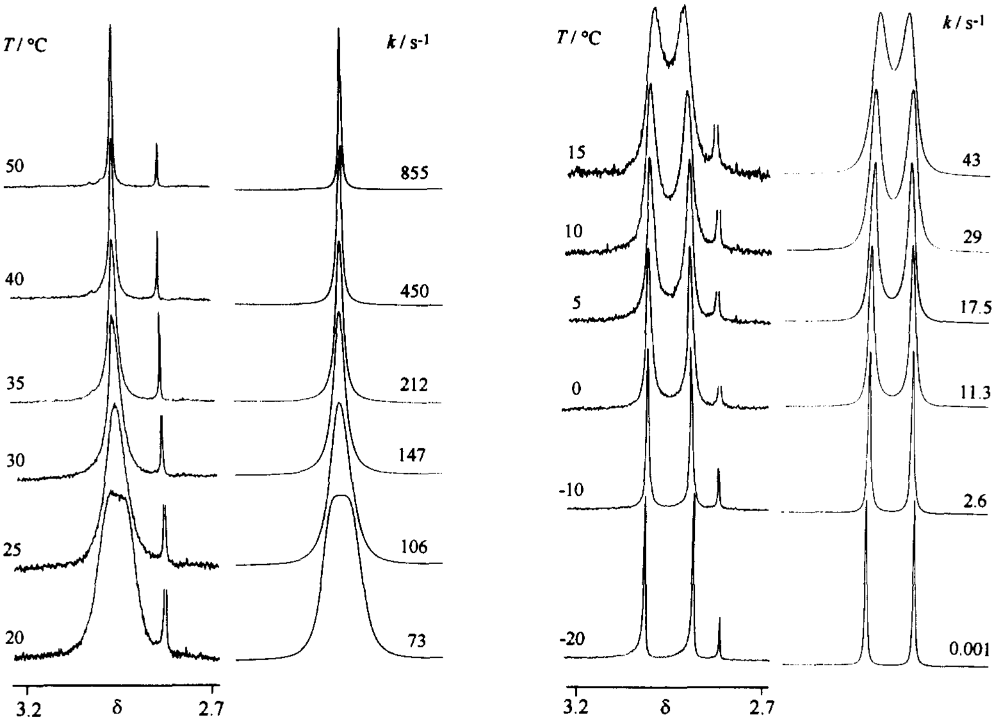


Fig. 1. 300 MHz ^{1}H NMR spectra of the methyl signals of [ReBr(CO)$_3$(DAP)] in CDCl$_3$ solution in the temperature range −20–50°C. Computer simulated spectra are shown on the right with "best-fit" rate constants for the fluxional process.

Table 3. Activation parameters for Re—O fluxion in [ReX(CO)$_3$(DAP)] complexes

X	Temperature range (°C)	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J K^{-1} mol^{-1})	$\Delta G^\ddagger$ (kJ mol^{-1})[a]
Cl	−20–60	64.2 ± 1.2	16.3 ± 4.3	59.4 ± 0.04
Br	−20–60	63.8 ± 1.8	9.1 ± 6.2	61.0 ± 0.05
I	−20–50	63.3 ± 1.7	6.5 ± 5.7	61.4 ± 0.04

[a] At 298.15 K.

Table 4. $\Delta G^\ddagger$ values for the 1,4-metallotropic shift of the ligand (L) in the complexes *fac*-[ReX(CO)$_3$L] (X = Cl, Br, I; L = 2,6-disubstituted pyridine)

2,6-Substituents	Donor atoms	Range of $\Delta G^\ddagger$ (kJ mol^{-1})	Source
Acetyl	ONO	59.4–61.5	This work
Pyrazol-1-yl	NNN	55.4–56.0	2
4-Methylpyrazol-1-yl	NNN	54.8–56.1	12
Pyridyl	NNN	70.3–73.0	10
3,5-Dimethylpyrazol-1-yl	NNN	70.4–77.3	2
Methylthiomethyl	SNS	75–81	11

nificantly different. The aim behind the solid state CP-MAS NMR studies was to examine whether any dynamic processes (*viz.* the 1,4-metallotropic shifts or rotation of the uncoordinated acetyl group) were occurring in the solid. The number of spectral lines clearly indicates the absence of any metallotropic shift, but there is some evidence that rotation of the pendant acetyl group occurs readily

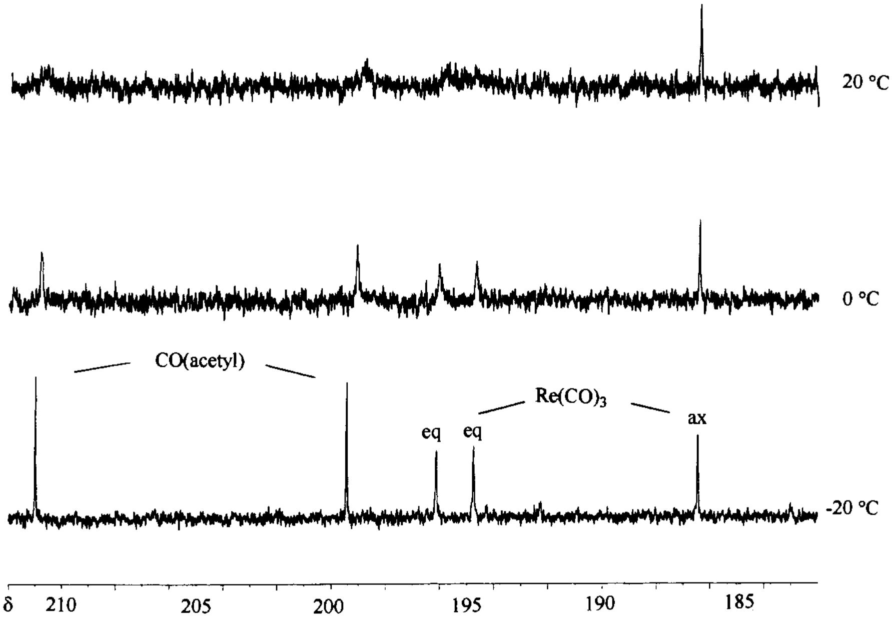


Fig. 2. The ^{13}C NMR spectra (carbonyl region) of [ReI(CO)$_3$(DAP)] at (a) -20, (b) 0 and (c) 20°C, showing broadening of the acetyl carbonyl signals and selective broadening of the metal carbonyls (equatorial signals only).

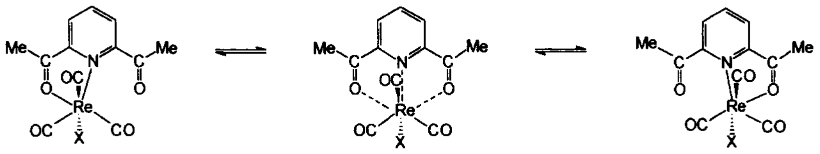


Fig. 3. The "tick–tock" twist mechanism of the 1,4-metallotropic shift.

at ambient temperatures but becomes severely restricted on cooling. At temperatures below *ca* -60°C the methyl carbon signal (Me$_E$) of the pendant acetyl group broadens significantly until at *ca* -80°C, the limiting low temperature, it is twice as broad as the methyl signal (Me$_A$) of the coordinated acetyl group. This strongly suggests the onset of dynamic broadening due to exchange between individual rotamers, but further investigations were beyond the low temperature limit of observation.

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