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Kinetics of the Combination of Methyl Ligands with Carbonyl or Isonitrile Ligands in Ruthenium(II) Complexes

David R. Saunders, Martin Stephenson, and Roger J. Mawby *
Department of Chemistry, The University of York, York YO1 5DD

Methyl complexes $[Ru(CO)_2MeR(PMe_2Ph)_2]$ [(1a), R = Ph; (1b), R = COMe; (1c), R = Me] react with Me_3CNC to form acetyl complexes $[Ru(CO)(CNCMe_3)(COMe)R(PMe_2Ph)_2]$, (2a)—(2c). The reaction rate is independent of isonitrile concentration, and the rate-determining step is believed to involve combination of methyl and carbonyl ligands. The reactions of complexes (1b) and (1c) are similar both in rate and in activation parameters, but for (1a) $\Delta H^{\ddagger}$ is appreciably lower and $\Delta S^{\ddagger}$ more negative: this may be due to increasing Ru–Ph π bonding in the approach to the transition state. Complex (2c) reacts with more Me_3CNC to form $[Ru(CO)(CNCMe_3)(COMe)\{C(NCMe_3)Me\}(PMe_2Ph)_2]$, (3c). Here the rate-determining step appears to involve combination of methyl and isonitrile ligands; this is much slower than combination of methyl and carbonyl ligands owing to a more negative $\Delta S^{\ddagger}$. In the absence of added Me_3CNC, complex (2c) slowly disproportionates into (1c) and (3c).

Recently we have reported the preparation of a range of complexes of ruthenium(II) containing two σ-bonded organic ligands.[1] Of these, three {of general formula $[Ru(CO)_2MeR(PMe_2Ph)_2]$} contained a methyl ligand; these were complexes (1a; R = Ph), (1b; R = COMe), and (1c; R = Me). All possessed structure (1) (see Scheme, where L = PMe_2Ph). Reactions of these complexes with CO in $CHCl_3$ led to the combination of methyl and carbonyl ligands to give products $[Ru(CO)_2(COMe)R(PMe_2Ph)_2]$, but the reactions of (1a) and (1b) went to equilibrium rather than completion.[1] We wished to obtain rate constants and activation parameters for the combination of methyl and carbonyl ligands, and therefore looked for reactions of (1a)—(1c) which would result in 100% conversion into acetyl complexes. Here we report on the kinetics of reactions of complexes (1a)—(1c) with Me_3CNC, which met this requirement, and also describe a further reaction involving combination of methyl and isonitrile ligands.

Results and Discussion

Characterization of Reaction Products.—Details of the i.r. and ^1H n.m.r. spectra of new complexes are given in Table 1, and ^{13}C n.m.r. data are listed in Table 2.

Treatment of a $CHCl_3$ solution of complex (1a) with an equimolar quantity of Me_3CNC resulted in a fairly rapid reaction. As in the case of the other reactions described here, it was not possible to isolate a solid product from the reaction, but it was clear from spectroscopic studies that a single product, (2a), had been formed in essentially quantitative yield. The i.r. spectrum of complex (2a) in $CHCl_3$ solution indicated the presence of isonitrile, carbonyl, and acyl ligands. Since the related complex $[Ru(CO)_2Ph_2(PMe_2Ph)_2]$ reacts with Me_3CNC to form $[Ru(CO)(CNCMe_3)(COPh)Ph(PMe_2Ph)_2]$,[2] it seemed likely that (2a) was either $[Ru(CO)(CNCMe_3)(COPh)Me(PMe_2Ph)_2]$ or $[Ru(CO)(CNCMe_3)(COMe)Ph(PMe_2Ph)_2]$, and it was clear from the ^1H and ^{13}C n.m.r. spectra that the latter formula was the correct one. It was also evident that the two PMe_2Ph ligands were mutually *trans*.† In the reaction of $[Ru(CO)_2Ph_2(PMe_2Ph)_2]$ with Me_3CNC, the isonitrile enters *trans* to the newly formed acyl ligand;[2] assuming that the stereochemistry of the reaction of complex (1a) with Me_3CNC was similar to this, we assigned structure (2) (see Scheme, where L = PMe_2Ph and R = Ph) to complex (2a). The reaction of complex (1b) with Me_3CNC followed the same pattern, and the product (2b) could be assigned the formula $[Ru(CO)(CNCMe_3)(COMe)_2(PMe_2Ph)_2]$ and the structure (2) (where L = PMe_2Ph and R = COMe) on the basis of the spectroscopic evidence.

Table 1. Infrared [a] and ^1H n.m.r.[b] spectra of new complexes

Complex	ν(C–N)/ cm^{-1}	ν(C–O)/ cm^{-1}	δ/p.p.m.	Assignment
(2a)	2 135	1 938	2.27 (s, 3)	COMe
		1 570	1.50 (t, 6)	PMe_2Ph
			1.25 (t, 6)	PMe_2Ph
			1.19 (s, 9)	$CNCMe_3$
(2b)	2 150	1 950	2.26 (s, 3)	COMe
		1 560	2.24 (s, 3)	COMe
			1.64 (t, 6)	PMe_2Ph
			1.51 (t, 6)	PMe_2Ph
			1.12 (s, 9)	$CNCMe_3$
(2c)	2 140	1 922	2.06 (s, 3)	COMe
		1 565	1.65 (t, 6)	PMe_2Ph
			1.55 (t, 6)	PMe_2Ph
			1.03 (s, 9)	$CNCMe_3$
			−0.46 (t, 3) [c]	RuMe
(3c)	2 160	1 985	2.22 (s, 3)	COMe
	1 690	1 555	1.73 (t, 6)	PMe_2Ph
			1.63 (t, 6)	PMe_2Ph
			1.49 (s, 9)	$CNCMe_3$
			1.38 (s, 3)	$C(NCMe_3)Me$
			1.32 (s, 9)	$C(NCMe_3)Me$

[a] In $CHCl_3$ solution. [b] In $CDCl_3$ solution. Only methyl proton resonances are listed. Multiplicities and relative areas are given after the chemical shift values. For PMe_2Ph methyl protons, $|^2J(P-H) + {}^4J(P-H)|$ = *ca.* 7 Hz. [c] $|^3J(P-H)|$ = 7.8 Hz.

Complex (1c) was also found to react with an equimolar quantity of Me_3CNC in $CHCl_3$ solution: the i.r. and n.m.r. spectra of the product (2c) showed it to be $[Ru(CO)(CNCMe_3)(COMe)Me(PMe_2Ph)_2]$. Thus (2c) still contained a methyl and a carbonyl ligand, raising the possibility that it might react with more Me_3CNC to form a diacetyl complex. If, however, complex (2c) also possessed structure (2), with R = Me in this instance, the remaining methyl and carbonyl ligands would be *trans* to one another, thus ruling out intramolecular combination to form a second acetyl ligand. When compound (2c) was treated with a further equimolar quantity of Me_3CNC in $CHCl_3$ solution, a slow reaction did occur to

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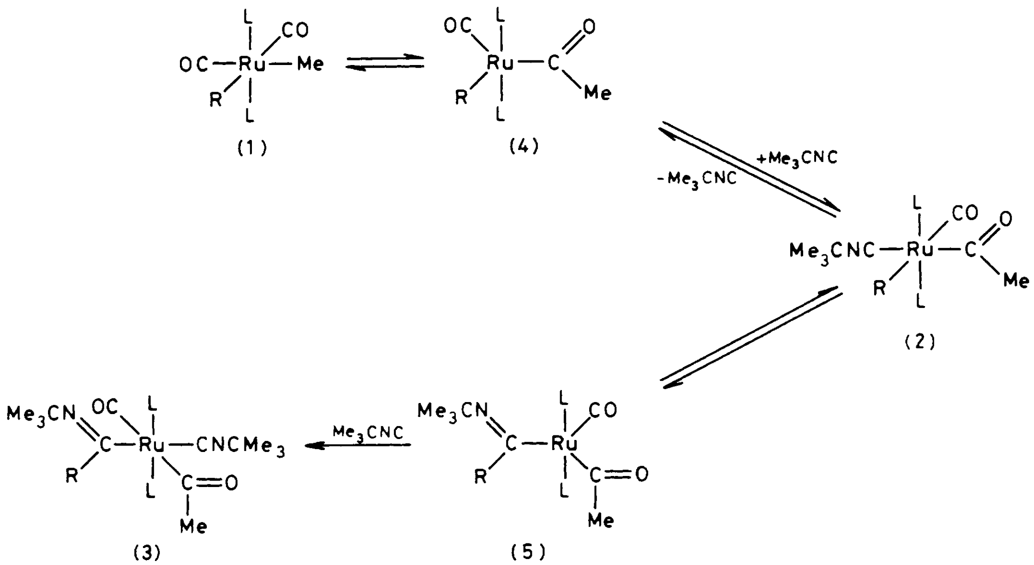
† The ways in which phosphorus ligands can be used as stereochemical probes in ruthenium(II) complexes have been described by Shaw and co-workers.[3,4]



Scheme. L = PMe_2Ph; R = Ph (a), COMe (b), or Me (c)

give a product (3c). It was, however, clear that (3c) was *not* simply $[Ru(CNCMe_3)_2(COMe)_2(PMe_2Ph)_2]$. Both its i.r. spectrum in $CHCl_3$ solution (C–O stretching band at 1 985 cm^{-1}) and its ^{13}C n.m.r. spectrum in $CDCl_3$ solution showed (3c) to contain a carbonyl ligand, and integration of its ^1H n.m.r. spectrum showed that the singlet resonance at δ 2.22 p.p.m. represented the protons of one acetyl group only, despite the fact that neither the ^1H nor the ^{13}C n.m.r. spectrum indicated the presence of a methyl ligand. The n.m.r. spectra contained two sets of resonances in the approximate positions expected for Me_3CNC ligands, *except* that only one ^{13}C resonance (at δ 144.8 p.p.m.) was observed in the region expected for the carbon atom directly attached to the metal.

We concluded that (3c) was $[Ru(CO)(CNCMe_3)(COMe)\{C(NCMe_3)Me\}(PMe_2Ph)_2]$, formed by combination of the methyl and isonitrile ligands in (2c) and occupation of the vacant co-ordination site by another molecule of isonitrile. The resonance for the carbon atom in the $-C(NCMe_3)Me$ ligand which was directly attached to the metal was observed at δ 242.1 p.p.m. and was a triplet $[|^2J(P-C)| = 13.8$ Hz]; by comparison, the resonance for the corresponding carbon atom in the acetyl ligand was a triplet $[|^2J(P-C)| = 11.5$ Hz] at δ 279.0 p.p.m. As mentioned above, the chemical shifts for the carbon and hydrogen atoms in the $NCMe_3$ unit were much the same as those for the corresponding atoms in the ' conventional ' isonitrile ligand, while the resonances for the carbon and hydrogen atoms in the remaining methyl group in the $-C(NCMe_3)Me$ ligand were singlets at δ 28.2 and 1.38 p.p.m. respectively. There are examples of similar reactions in the literature,[5-7] and, although we have been unable to find ^{13}C n.m.r. data for complexes containing ligands of the type $-C(NR)R'$, we note that the proton resonance for the carbon-bonded methyl group in $[Pt\{C(NMe)Me\}I(PPh_3)_2]$ is at δ 1.47 p.p.m., and that the i.r. spectrum of this complex includes a C–N stretching band at 1 620 cm^{-1} [for (3c) the corresponding band is at 1 690 cm^{-1}].[8]

The stereochemistry shown for (3c) in the Scheme (where L = PMe_2Ph and R = Me) is based on the assumption that the new Me_3CNC ligand enters *trans* to the $-C(NCMe_3)Me$ ligand, but attack *trans* to the acetyl ligand [as in the conversion of (1a)—(1c) into (2a)—(2c)] certainly cannot be ruled out.

As mentioned above, the reaction of equimolar quantities of complex (1c) and Me_3CNC initially resulted in essentially quantitative conversion into (2c). When (2c) was left in solution, however, it slowly disproportionated into (1c) and (3c), thus establishing the reversibility of the original reaction between (1c) and Me_3CNC. Unlike (2c), complexes (2a) and (2b) did not react with more Me_3CNC, and did not disproportionate in solution.

Kinetic Studies.—The reactions of complexes (1a)—(1c) with Me_3CNC to form (2a)—(2c) and the further reaction of (2c) to yield (3c) were all monitored by i.r. spectroscopy. The solvent used for most of the studies was $CHCl_3$, since this had been used for the preparative work and i.r. characterization of the products. All the kinetic runs were carried out with Me_3CNC in large excess, so that its concentration could be regarded as remaining constant throughout a given run. In the reaction of (1c), conversion into (2c) was essentially complete before any (3c) was observed, and disproportionation of (2c) was completely suppressed by the presence of excess of Me_3CNC.

Preliminary studies established that all the reactions were first order in the concentration of ruthenium complex, and that rate constants were unaffected by variation in the initial concentration of the complex. As a check on the reproducibility of rate constant values obtained by the i.r. techinque, a set of three supposedly identical kinetic runs was carried out for the reaction of complex (1c) with Me_3CNC to form (2c). The three values for the rate constant were all within 2% of the mean value.

First-order rate constants for all the reactions studied are listed in Table 3. Each complex [(1a)—(1c) and (2c)] reacted with Me_3CNC at a rate which was essentially independent of the concentration of isonitrile, indicating that the rate-determining step under the conditions used did not involve the isonitrile. The likely explanation of this kinetic behaviour (see Scheme) is that the slow step involves combination of methyl and carbonyl ligands to give (4) [or, in the case of the reaction of (2c), combination of methyl and isonitrile ligands to give (5)], and that the subsequent attack by Me_3CNC is appreciably faster than either the formation of (4) and (5) or their reconversion into (1a)—(1c) and (2c) respectively.

Plots of ln k against T^{-1} were used both to determine rate constants at a common temperature (298.3 K) and to obtain

Table 2. Carbon-13 n.m.r. spectra of new complexes *

Complex	δ/p.p.m.	Assignment	Coupling constant/Hz	Assignment
(2a)	272.5 (t)	*C*OMe	12.0	$\lvert{}^2J(P-C)\rvert$
	200.9 (t)	RuCO	9.2	$\lvert{}^2J(P-C)\rvert$
	165.7 (t)	RuPh (C^1)	16.0	$\lvert{}^2J(P-C)\rvert$
	151.4 (br)	*C*NCMe$_3$		
	142.9 (t)	RuPh (C^2)	2.7	$\lvert{}^3J(P-C)\rvert$
	125.3 (s)	RuPh (C^3)		
	121.1 (s)	RuPh (C^4)		
	55.8 (s)	CN*C*Me$_3$		
	53.1 (t)	CO*Me*	2.3	$\lvert{}^3J(P-C)\rvert$
	30.4 (s)	CNC*Me*$_3$		
	15.4 (t)	P*Me*$_2$Ph	30.2	$\lvert{}^1J(P-C) + {}^3J(P-C)\rvert$
	14.5 (t)	P*Me*$_2$Ph	32.0	$\lvert{}^1J(P-C) + {}^3J(P-C)\rvert$
(2b)	276.6 (t)	*C*OMe	12.8	$\lvert{}^2J(P-C)\rvert$
	275.0 (t)	*C*OMe	11.9	$\lvert{}^2J(P-C)\rvert$
	201.6 (t)	RuCO	10.5	$\lvert{}^2J(P-C)\rvert$
	151.0 (br)	*C*NCMe$_3$		
	56.1 (s)	CN*C*Me$_3$		
	50.1 (s)	CO*Me*		
	49.1 (s)	CO*Me*		
	29.9 (s)	CNC*Me*$_3$		
	16.9 (t)	P*Me*$_2$Ph	31.1	$\lvert{}^1J(P-C) + {}^3J(P-C)\rvert$
	15.3 (t)	P*Me*$_2$Ph	31.1	$\lvert{}^1J(P-C) + {}^3J(P-C)\rvert$
(2c)	274.5 (t)	*C*OMe	12.8	$\lvert{}^2J(P-C)\rvert$
	198.6 (t)	RuCO	10.1	$\lvert{}^2J(P-C)\rvert$
	154.6 (br)	*C*NCMe$_3$		
	55.6 (s)	CN*C*Me$_3$		
	51.1 (s)	CO*Me*		
	30.3 (s)	CNC*Me*$_3$		
	16.1 (t)	P*Me*$_2$Ph	29.3	$\lvert{}^1J(P-C) + {}^3J(P-C)\rvert$
	13.9 (t)	P*Me*$_2$Ph	29.3	$\lvert{}^1J(P-C) + {}^3J(P-C)\rvert$
	−6.0 (t)	Ru*Me*	11.4	$\lvert{}^2J(P-C)\rvert$
(3c)	279.0 (t)	*C*OMe	11.5	$\lvert{}^2J(P-C)\rvert$
	242.1 (t)	*C*(NCMe$_3$)Me	13.8	$\lvert{}^2J(P-C)\rvert$
	200.0 (t)	RuCO	10.0	$\lvert{}^2J(P-C)\rvert$
	144.8 (br)	*C*NCMe$_3$		
	59.3 (s) 58.4 (s)	C(N*C*Me$_3$)Me CN*C*Me$_3$		
	52.5 (s)	CO*Me*		
	30.1 (s) 29.7 (s)	C(NC*Me*$_3$)Me CNC*Me*$_3$		
	28.2 (s)	C(NCMe$_3$)*Me*		
	16.9 (t)	P*Me*$_2$Ph	33.0	$\lvert{}^1J(P-C) + {}^3J(P-C)\rvert$
	16.1 (t)	P*Me*$_2$Ph	31.0	$\lvert{}^1J(P-C) + {}^3J(P-C)\rvert$

* In CDCl$_3$ solution. Resonances due to PMe$_2$Ph phenyl carbon atoms omitted. Multiplicities are given after the chemical shift values; br = broad.

activation parameters for the reactions (see Table 4). From the data in Table 4, it can be seen that the reactions of complexes (1b) and (1c) are similar both in rate and in $\Delta H^\ddagger$, indicating that it makes little difference whether the organic ligand not involved in the reaction is acetyl or methyl. In both instances $\Delta S^\ddagger$ is relatively small.

Although the *rate* of reaction of complex (1a) at 298.3 K does not differ greatly from those for (1b) and (1c) at the same temperature, the activation parameters are strikingly different. The presence of the phenyl ligand in (1a) greatly reduces $\Delta H^\ddagger$, but at the expense of a fairly large negative $\Delta S^\ddagger$. Here and in the case of the reaction of (2c), which also has a sizeable negative entropy of activation, evidence of solvent participation in the reaction was sought by changing the solvent to propanone, which has a higher dielectric constant and is a better ligand than CHCl$_3$. In neither case, however, did this change of solvent have a very marked effect on reaction rate (see Table 3), each reaction being in fact a little *slower* in propanone than in CHCl$_3$.

If the differences in activation parameters between the reaction of complex (1a) and those of (1b) and (1c) are not the result of greater solvent participation, they may alternatively be due to π bonding between metal and phenyl ligand. *X*-Ray investigation of the structure of [Ru(CO)(CNCMe$_3$)Ph(Cl)(PMe$_2$Ph)$_2$] has revealed that the phenyl ligand is positioned so that its π system overlaps with the *d* orbital which (although shared by the isonitrile ligand *trans* to it) is *not* shared by the strongly π-accepting carbonyl ligand which lies *cis* to it.[9] By adopting the same orientation (with its ring coplanar with the carbonyl and methyl ligands), the phenyl ligand in (1a) can take advantage of the fact that the carbonyl ligand *trans* to it becomes involved in the rearrangement to form the acetyl ligand. Thus it may well be that the metal–phenyl bond becomes *stronger* in the approach to the activated state, but at the expense of increased restriction of rotation of the phenyl ligand.*

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* A referee doubts whether increased restriction of rotation of the aryl ligand could cause such a large negative $\Delta S^\ddagger$. We share his doubts, but there is no obvious alternative explanation.

Table 3. Kinetic data for reactions of complexes (1a)—(1c) and (2c) with Me_3CNC [a]

Complex	T/K	10^3[complex]	$10^3[Me_3CNC]$	$10^4k_{obs.}/s^{-1}$
		mol dm^{-3}		
(1a)	283.4	4.43	88.6	11.5(4)
	288.8	3.81	76.2	18.0(2)
	292.9	4.41	88.2	25.9(3)
	298.3	5.90	59.0	39.6(4)
	298.3	5.90	118.0	38.7(6)
	298.3	5.90	177.0	39.9(3)
(1b)	288.1	4.63	92.6	5.23(7)
	293.2	5.03	100.6	9.57(12)
	298.4	4.83	48.3	16.6(1)
	298.4	4.83	96.6	17.1(3)
	298.4	4.83	144.9	15.7(3)
	304.0	4.83	96.6	33.7(4)
(1c)	288.8	4.32	86.4	5.01(10)
	292.9	4.53	90.6	9.58(14)
	298.3	6.91	69.1	16.2(1)
	298.3	6.91	138.2	15.3(1)
	298.3	6.91	207.3	16.6(2)
	303.6	4.07	81.4	32.7(1)
(2c)	311.5	6.04	120.8	0.573(8)
	316.8	5.61	56.1	0.799(2)
	316.8	5.61	112.2	0.838(7)
	316.8	5.61	168.3	0.805(10)
	322.5	6.25	125.0	1.27(2)
	327.4	6.47	129.4	1.95(3)
(1a) [b]	298.3	4.57	91.4	22.6(4)
(2c) [b]	316.8	6.03	120.6	0.597(10)

[a] Reactions were carried out in $CHCl_3$ solution except where stated otherwise. Standard deviations, given in parentheses, refer to the final figure(s) of the values given for the rate constants. [b] In propanone solution.

Complexes (1b) and (2c) differ only in one ligand, but this is the one which combines with the methyl ligand in the reactions to form (2b) and (3c) respectively. The reaction of (2c), where the ligand involved is Me_3CNC, is *ca.* 100 times slower at 298.3 K than that of (1b), where the ligand involved is CO. Despite this, $\Delta H^\ddagger$ is appreciably *lower* for complex (2c) than for (1b), and the lower rate for the reaction of (2c) is attributable to the much more negative $\Delta S^\ddagger$. This may be linked to changes in bonding and loss of freedom of movement within the isonitrile ligand as the combination with the methyl ligand occurs. Otsuka and Ataka [10] have reported that $\Delta S^\ddagger$ for the combination of methyl and isonitrile ligands in $[PdMeI(CNCMe_3)_2]$ is also fairly large and negative (-92 J K^{-1} mol^{-1}).

Experimental

The methods used to prepare complexes (1a)—(1c) have been described in an earlier paper.[1] The reactions of (1a)—(1c) with Me_3CNC to form (2a)—(2c) were carried out in $CHCl_3$ solution, using concentrations of each reactant of *ca.* 1.5×10^{-2} mol dm^{-3}, and were monitored by recording the i.r. spectra of samples of the solutions at appropriate intervals. When the reactions were complete, the solvent was removed under reduced pressure, and the products were dissolved in $CDCl_3$ so that their n.m.r. spectra could be obtained. The reactions were also carried out in $CDCl_3$ solutions, working with concentrations of each reactant of *ca.* 0.15 mol dm^{-3}, and monitored by ^1H n.m.r. spectroscopy. The final spectra were then checked against those of the products obtained from $CHCl_3$ solution. The reaction of complex (2c) with Me_3CNC was studied by the same techniques but using a 1 : 2 molar ratio of (1c) to Me_3CNC, so that (2c) was formed and then reacted with the second mole of isonitrile.

Table 4. Activation data at 298.3 K *

Complex	$10^4k/s^{-1}$	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta G^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
(1a)	39.6	56(1)	87	-104
(1b)	16.9	81(3)	89	-26
(1c)	16.8	85(4)	89	-12
(2c)	0.176	64(3)	100	-123

* For reactions in $CHCl_3$ solution. Standard deviations, given in parentheses, refer to the final figure of the values given for the enthalpies of activation. Errors in values of k and $\Delta G^\ddagger$ reflect those listed in Table 3.

Solutions for the kinetic runs were made up under nitrogen in flasks kept in a thermostatically controlled water-bath, using solvents (already at bath temperature) which had been purged with nitrogen to remove all oxygen. Samples were withdrawn at intervals, and their absorbance at a selected wavenumber was recorded on a Perkin-Elmer PE177 spectrophotometer. The wavenumber chosen corresponded to the highest energy C–O stretching band in the spectrum of each of the reactant ruthenium complexes [(1a), 2 002; (1b), 2 013; (1c), 1 999 cm^{-1}], except in the case of the conversion of (2c) into (3c), where the growth of the band at 1 985 cm^{-1} in the spectrum of (3c) was monitored. Data were collected for between 2.5 and 3.0 half-lives, and rate constants were obtained by least-mean-squares treatment of values for ln A [or, in the case of (2c) $\longrightarrow$ (3c), ln $(A_\infty - A)$] and time. At the end of the kinetic runs, the i.r. spectra of the solutions were checked against those obtained for (2a)—(2c) and (3c) from the reactions of (1a)—(1c) with stoicheiometric quantities of Me_3CNC. In the case of the runs in propanone solution, the propanone was removed under reduced pressure and the product was redissolved in $CHCl_3$ so that its i.r. spectrum could be checked.

Details of the instruments used to obtain n.m.r. spectra have been given elsewhere.[1]

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