trans-Dichlorotetrakis(pyridine)platinum(IV) Nitrate: a Classical Co-ordination Compound

Kenneth R. Seddon* and **Janet E. Turp**
School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ
Edwin C. Constable
University Chemistry Laboratory, Lensfield Road, Cambridge CB2 1EW
Ole Wernberg*
Department of Chemistry, Odense University, DK-5230 Odense M, Denmark

Claims that *trans*-dichlorotetrakis(pyridine)platinum(IV) nitrate forms a covalent hydrate when dissolved in water are shown to be in error; the observed acidity of the aqueous solution is due to the presence of a small amount of a strongly acidic impurity, and all of the observed physical and spectroscopic properties of the salt are simply interpreted in terms of classical co-ordination chemistry.

The theory of covalent hydration (or, more generally, pseudobase formation)[1] for di-imine ligands, such as 2,2′-bipyridine and 1,10-phenanthroline, co-ordinated to transition-metal ions is currently the subject of much criticism, and the arguments (both for and against the theory) have been reviewed recently.[2-5] There have been only three claims that pyridine complexes may exist as covalent hydrates, and these reports relate to salts of *cis*-$[Ru(bipy)_2(py)_2]^{2+}$ (py = pyridine, bipy = 2,2′-bipyridine),[6] *trans*-$[Pt(py)_4Cl_2]^{2+}$,[7] and *trans*-$[Rh(py)_4Cl_2]^{+}$,[7,8] The first of these complexes has now been characterised by two-dimensional ^1H n.m.r. spectroscopy and single-crystal *X*-ray diffraction (as its tetrafluoroborate salt), and is the subject of a separate paper.[9] Testing the claims for the last of these complexes (that its anti-bacterial action originates with its ability to form covalent hydrates) represents a koan, as assertions of this type are essentially unconfirmable, and rely completely on the validity of the claims for the other two complexes; the claims concerning *trans*-$[Pt(py)_4Cl_2][NO_3]_2$ are the subject of the present report and two preliminary communications.[10,11] In neither *cis*-$[Ru(bipy)_2(py)_2]^{2+}$ nor *trans*-$[Pt(py)_4Cl_2]^{2+}$ do we find any evidence to support the existence of a covalently hydrated compound. Indeed, there were no experimental observations which could not be accounted for by considering the complexes as classical co-ordination compounds.

Experimental

General Procedures.—^1H N.m.r. spectra were recorded using a Bruker WH-300 and ^{13}C and ^{195}Pt n.m.r. spectra were recorded with a Bruker WH-400 spectrometer. All chemical shifts are defined as positive to low field (high frequency) of the reference compound. Proton and carbon-13 chemical shifts were measured relative to tetramethylsilane.

Preparation of cis-*Dichlorobis(pyridine)platinum*(II).—A solution of pyridine (0.77 g, 9.7 mmol) in water (5 cm^3) was added to a continuously stirred solution of potassium tetrachloroplatinate(II) (2.0 g, 5.2 mmol) in water (20 cm^3). An off-white precipitate began to form after a short time (*ca.* 15 min), and after 6 h precipitation was complete. The precipitate was collected by filtration, washed with iced water (3 × 10 cm^3) to remove potassium chloride, and dried *in vacuo* (Found: C, 28.35; H, 2.35; Cl, 16.65; N, 6.50. Calc. for $C_{10}H_{10}Cl_2N_2Pt$: C, 28.30; H, 2.35; Cl, 16.70; N, 6.60%).

Preparation of trans-*Dichlorotetrakis(pyridine)platinum*(IV) *Nitrate according to a Literature Method.*—This complex was prepared according to the method of Grinberg *et al.*[12] *cis*-Dichlorobis(pyridine)platinum(II) (1 g, 2.4 mmol) and pyridine (1.72 g, 21.8 mmol) were mixed in water (5 cm^3) and heated until dissolution was complete. The solution {now containing $[Pt(py)_4]^{2+}$} was then cooled to room temperature, and any insoluble residue removed by filtration. The filtrate was then heated for 5 min (care being taken that the temperature did not exceed 100 °C), and poured into a pre-heated solution of concentrated nitric acid (10 cm^3) in water (5 cm^3) to produce a yellow solution. Heating was continued (*ca.* 75 °C) for 30 min. The mixture was then cooled to room temperature, and any insoluble residue removed by filtration. The filtrate was mixed with twice its own volume of ethanol and a large excess (*ca.* 500 cm^3) of diethyl ether, cooled to 4 °C, and left overnight, whence a yellow solid precipitated. This precipitate was collected by filtration and washed with ethanol–diethyl ether (*ca.* 2 l; 1:3 v/v).

The analysis figures for several preparations of this salt vary considerably, and are discussed in the main text. All samples produced acidic solutions in water.

Preparation of Pure trans-*Dichlorotetrakis(pyridine)platinum*(IV) *Nitrate.*—*cis*-Dichlorobis(pyridine)platinum(II) (1.88 g, 4.4 mmol) and pyridine (2 g, 25.3 mmol) were mixed in water (25 cm^3) and heated at 100 °C, with stirring, until dissolution was complete. The solution {now containing $[Pt(py)_4]^{2+}$} was then cooled to room temperature, and any insoluble residue removed by filtration. The filtrate was added, over a few minutes, to a boiling mixture of concentrated nitric acid (10 cm^3) and water (5 cm^3), and heating was continued for 30 min. The volume of the solution was then reduced to 5 cm^3 by distillation under reduced pressure and cooled to room temperature. Ethanol (50 cm^3) was added to the solution, and this mixture was then added to an excess of diethyl ether (1 l), causing the precipitation of a mixture of pyridinium nitrate and *trans*-$[Pt(py)_4Cl_2][NO_3]_2$. This suspension was cooled to −10 °C for 1 h prior to collecting the crude product by filtration. The bright yellow solid was washed with a solution of ethanol in diethyl ether (5 cm^3, 30%), and then added to an excess of the same solvent mixture (500 cm^3). The suspension was stirred for 10 min, and the yellow product collected by filtration and washed with a solution of ethanol in diethyl ether (3 × 5 cm^3, 30%), and finally diethyl ether (5 cm^3), and then dried in air (Found: C, 34.0; H, 2.85; Cl, 9.7; N, 11.85; Pt, 27.3. Calc. for $C_{20}H_{20}Cl_2N_6O_6Pt$: C, 34.00; H, 2.85; Cl, 10.05; N, 11.90; Pt, 27.60%).

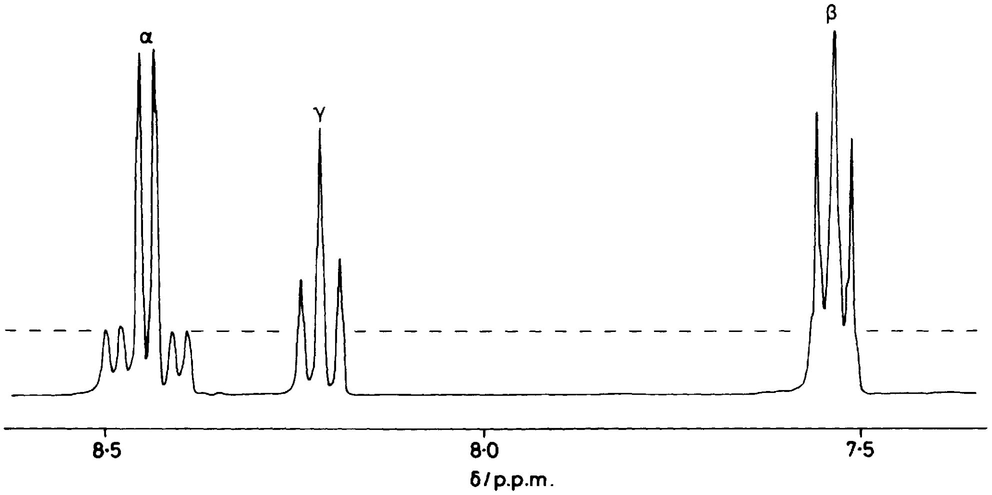


Figure 1. The ^1H n.m.r. (300.13 MHz) spectrum of $[Pt(py)_4Cl_2][NO_3]_2$ in D_2O. The dotted line represents the level of signal expected for the presence of *ca.* 18% of covalent hydrate

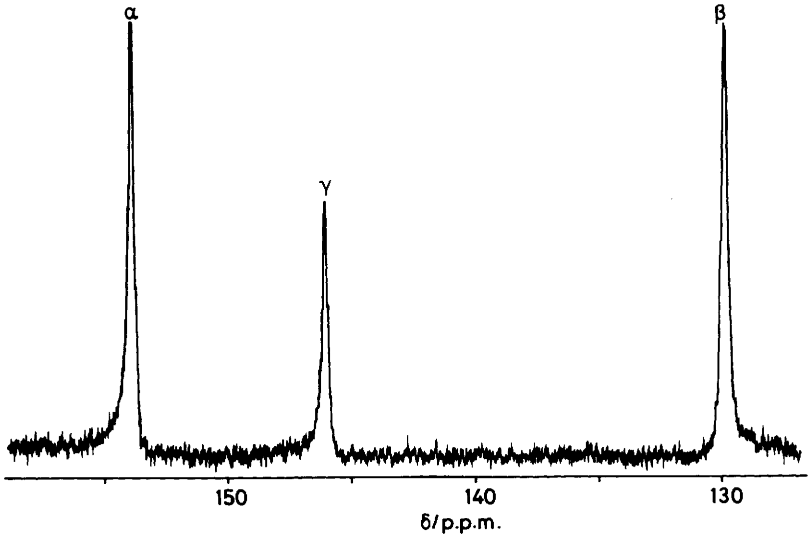


Figure 2. The ^{13}C n.m.r. (100.484 MHz) spectrum of $[Pt(py)_4Cl_2][NO_3]_2$ in D_2O

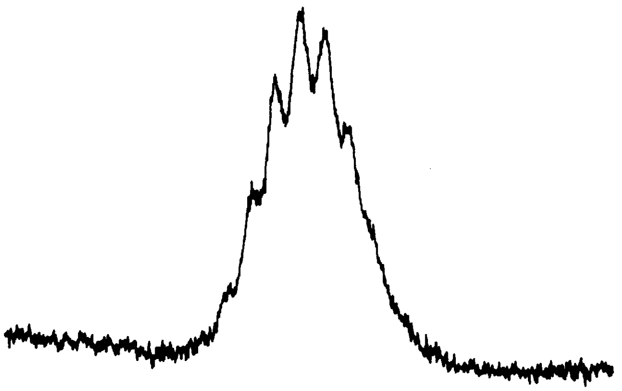


Figure 3. The ^{195}Pt n.m.r. (89.56 MHz) spectrum of $[Pt(py)_4Cl_2][NO_3]_2$ in D_2O

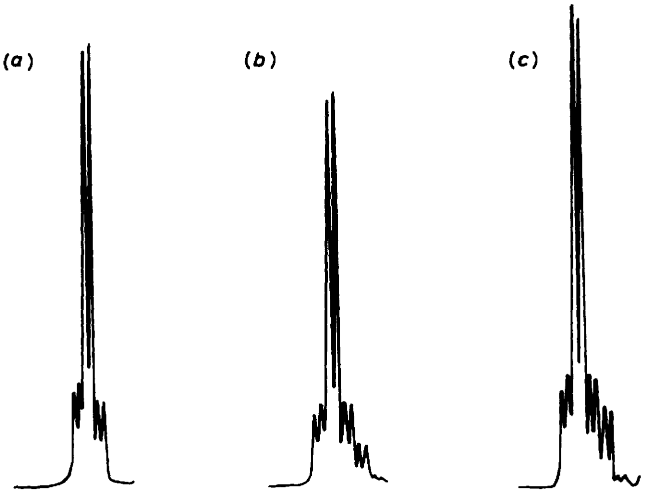
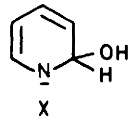


Figure 4. The change in the low-field (H_α) signal in the ^1H n.m.r. (300.13 MHz) spectrum of $[Pt(py)_4Cl_2][NO_3]_2$ in D_2O with time; (*a*) a freshly prepared solution, (*b*) after 17 d, and (*c*) after 66 d

Results and Discussion

In 1981, Gillard and Wademan[7] claimed that a salt previously reported by Hedin[13] and Grinberg *et al.*[12] as *trans*-$[Pt(py)_4Cl_2][NO_3]_2$ undergoes covalent hydration in aqueous solution to form *trans*-$[Pt(py)_3(X)Cl_2]^+$ (X = 2-hydroxy-1,2-



X

dihydro-1-pyridyl) according to equation (1). The sole piece of experimental evidence quoted to support this claim (which is all

$$[Pt(py)_4Cl_2]^{2+} + H_2O \rightleftharpoons [Pt(py)_3(X)Cl_2]^+ + H^+ \quad (1)$$

the more remarkable as there is no evidence for the covalent hydration of the *N*-methylpyridinium cation[14]) was the observation that a 10^{-2} mol dm^{-3} aqueous solution of *trans*-$[Pt(py)_4Cl_2][NO_3]_2$ has a pH of 2.87. A value for the apparent acid dissociation constant, *K*, of *trans*-$[Pt(py)_4Cl_2]^{2+}$ [as

$$K = \frac{[Pt(py)_3(X)Cl_2{}^+][H^+]}{[Pt(py)_4Cl_2{}^{2+}]} \quad (2)$$

defined by equation (2)] of $10^{-3.4}$ at 25 °C was quoted.[7] These conclusions were immediately refuted by Mønsted and Nord,[15] and that refutation was dismissed by Gillard and Wademan.[16]

From the *K* value quoted by Gillard and Wademan,[7] it follows that 18% of the platinum complex should be present in aqueous solution as the covalent hydrate. We thus prepared the complex salt $[Pt(py)_4Cl_2][NO_3]_2$ according to the literature route,[12] and recorded its ^1H (Figure 1), ^{13}C (Figure 2) and ^{195}Pt (Figure 3) n.m.r. spectra in D_2O. As can be clearly seen, only one n.m.r. active species is present in any significant concentration, and its spectroscopic parameters in D_2O [$\delta(H_\alpha)$ 8.45, $\delta(H_\beta)$ 7.54, $\delta(H_\gamma)$ 8.23 p.p.m., $^3J(H_\alpha H_\beta)$ 5.9, $^4J(H_\alpha H_\gamma)$ 1.3, $^3J(H_\beta H_\gamma)$ 7.2, $^3J(PtH_\alpha)$ 26 Hz, assignments confirmed by irradiation at H_β; $\delta(C_\alpha)$ 154.1, $\delta(C_\beta)$ 130.2, $\delta(C_\gamma)$ 146.3 p.p.m.] are entirely consistent with it being $[Pt(py)_4Cl_2]^{2+}$, and confirm its *trans* geometry. In particular, there are no resonances in the regions of the ^1H and ^{13}C n.m.r. spectra associated with covalent hydration, and only one signal is observed in the ^{195}Pt n.m.r. spectrum. The level of the ^1H n.m.r. signal expected for the 18% of covalent hydrate is marked by the broken line in Figure 1. Gaussian enhancement of the spectrum shown in Figure 1 allows a weak signal on the high-field edge of the H_α signal to be detected (Figure 4). This increases in intensity with time, developing detectable platinum satellites, and probably coincides with the slow generation of $[Pt(py)_4(OH)Cl]^{2+}$, as reported by Grinberg *et al.*[12]

$$[Pt(py)_4Cl_2]^{2+} + H_2O \rightleftharpoons [Pt(py)_4(OH)Cl]^{2+} + H^+ + Cl^- \quad (3)$$

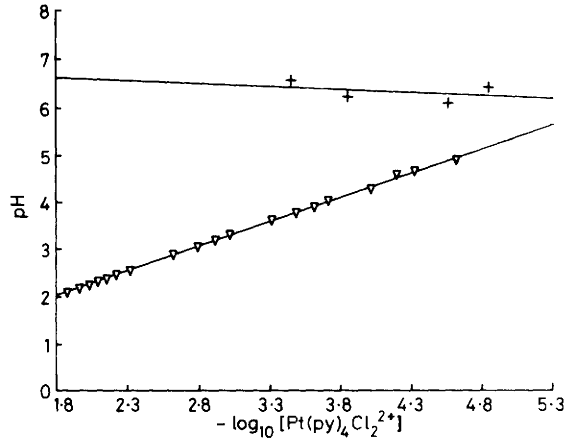


Figure 5. A graph of pH *versus* $-\log_{10}[Pt(py)_4Cl_2{}^{2+}]$ for solutions of $[Pt(py)_4Cl_2][NO_3]_2$ in water. The points plotted as ▽ are for the complex prepared according to Grinberg *et al.*,[12] and those plotted as + are for the highly purified complex. The straight lines were fitted to the experimental data by a conventional least-squares linear regression procedure

Table. Analytical and pH data for $[Pt(py)_4Cl_2][NO_3]_2 \cdot xHNO_3$

	Analysis[a] (%)					
x	C	H	Cl	N	pH[a,b]	Ref.
0.00	34.0 (34.00)	2.85 (2.85)	9.7 (10.05)	11.85 (11.90)	6.5 (7.0)	This work
0.17	33.5 (33.50)	2.85 (2.85)	— (9.90)	12.0 (12.05)	2.85[c] (2.75[c])	16
0.40	32.8 (32.85)	2.75 (2.80)	9.7 (9.70)	12.05 (12.25)	2.2[c] (2.4[c])	This work
					3.3 (3.4)	This work
0.008			10.20 (10.05)		5.1 (5.1)	12

[a] Calculated values in parentheses. [b] The pH of a 10^{-3} mol dm^{-3} aqueous solution, unless otherwise stated. [c] The pH of a 10^{-2} mol dm^{-3} aqueous solution.

At the time of dissolution of the complex, the hydrolysed cation was present to an extent of 0.8%. This raised the possibility that the undisputed acidity observed by ourselves (typically pH 4.2 at 10^{-3} mol dm^{-3}), Grinberg (pH 5.1 at 10^{-3} mol dm^{-3}), and Gillard (pH 2.87 at 10^{-2} mol dm^{-3}) arose not from a covalent hydrate, but from the presence of a strongly acidic impurity in the isolated complex. This suggestion is clearly not ludicrous, as the product is formed in concentrated nitric acid solution {and many salts of the hydrogendinitrate ion, $[H(ONO_2)_2]^-$, are known[17]}, and only a low level of impurity would be needed to produce the observed acidity. This hypothesis was tested by studying the pH of aqueous solutions of *trans*-$[Pt(py)_4Cl_2][NO_3]_2$ as a function of concentration. For the presence of a strongly acidic impurity, $[H^+] \propto$ [complex], and so $[H^+] = K'$[complex]; hence, equation (4).

$$pH = -\log_{10}[complex] + constant \quad (4)$$

Thus, a graph of pH *versus* $-\log_{10}$[complex] would have a unit gradient. If Gillard's theory of covalent hydration were correct, however, then equation (2) would yield: $[H^+]^2 = K$[complex], and hence, equation (5). A graph of pH *versus* $-\log_{10}$[com-

$$pH = -\tfrac{1}{2}\log_{10}[complex] + constant \quad (5)$$

plex], under the assumptions of equation (5), would have a gradient of 0.5. The results of our experimental observations are plotted (as ▽) in Figure 5, and the slope of 1.03 agrees with equation (4), unambiguously supporting the hypothesis that the acidity is due to the presence of a strongly acidic impurity, as suggested by Mønsted and Nord.[15] The ^1H n.m.r. evidence shows that the concentration of $[Pt(py)_4(H_2O)Cl]^{3+}$ would be far too small to account for this level of acidity, and so the most likely identity of the contaminant is $[H(ONO_2)_2]^-$. This is

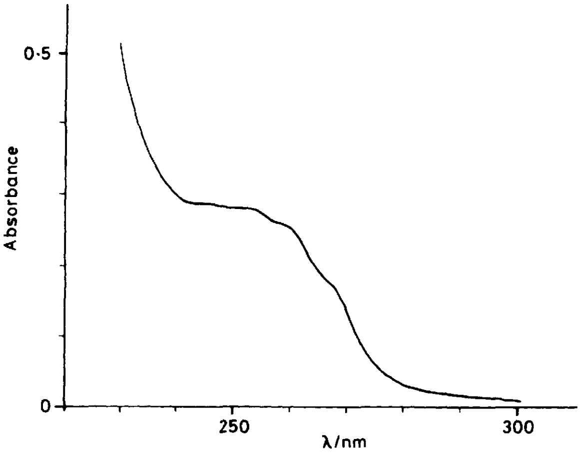


Figure 6. The electronic absorption spectrum of highly purified *trans*-$[Pt(py)_4Cl_2][NO_3]_2$ in water (2.29×10^{-5} mol dm^{-3})

borne out by our own, and the published,[12,16] analytical data, which fit the formula $[Pt(py)_4Cl_2][NO_3]_2{\cdot}xHNO_3$ rather well (see Table), and it is of interest to note that the original report, in 1886,[13] of a platinum(IV) complex in this system formulates the compound as $[Pt(py)_4Cl_2][NO_3]_2{\cdot}2HNO_3{\cdot}\,2H_2O$. Moreover, the predicted and observed pH values for the solutions, from all workers, are in excellent agreement with this formulation (see Table).

If, during the preparation, a higher pyridine concentration is used, products contaminated with pyridinium nitrate are formed: this by-product is immediately detectable by microanalysis and i.r. and ^1H n.m.r. spectroscopy. This contaminant is not present in any of the samples discussed in this paper.

Furthermore, a slightly modified preparation of the complex (see Experimental section) produces a pure salt (with excellent microanalytical data) which gives an aqueous solution of pH 6.5 at 3.45×10^{-4} mol dm^{-3}: this pH is essentially invariant with concentration (see Figure 5, points plotted as +). Moreover, the electronic spectrum of this salt in water (Figure 6) obeys the Beer–Lambert law (in the range 10^{-3}—10^{-5} mol dm^{-3}) over a pH range of 2—8, confirming again that no significant equilibrium of the type shown in equation (1) can exist in solution. At higher pH, reduction of the cation occurs.[18]

In conclusion, we can find no evidence to support the claims of Gillard and Wademan[7] that hydroxide ion readily adds to the co-ordinated *N*-heterocycles in *trans*-$[Pt(py)_4Cl_2]^{2+}$. As this is one of the few systems in which the literature claims of covalent hydration can be empirically tested, and these claims have been demonstrated here to be erroneous, the importance of the criteria of Albert and Armarego[19] for establishing the existence of covalent hydrates is highlighted. Albert and Armarego proposed that *at least three* physical techniques should indicate the existence of covalent hydrates before their existence was considered proven, and this proposition was for organic systems in which their formation was not considered to be polemical. As there are still, *pace* Gillard, no proven examples of complexes of 2,2′-bipyridine, 1,10-phenanthroline, or pyridine forming covalent hydrates, any future claims must be supported by unassailable evidence if the theory is to maintain any vestige of credibility.

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References

1 R. D. Gillard, *Coord. Chem. Rev.*, 1975, **16**, 67.
2 E. C. Constable, *Polyhedron*, 1983, **2**, 551.
3 N. Serpone, *Coord. Chem. Rev.*, 1983, **50**, 209.
4 R. D. Gillard, *Coord. Chem. Rev.*, 1983, **50**, 303.
5 G. Nord, *Comm. Inorg. Chem.*, 1985, **4**, 193.
6 R. D. Gillard and C. T. Hughes, *J. Chem. Soc., Chem. Commun.*, 1977, 776.
7 R. D. Gillard and R. J. Wademan, *J. Chem. Soc., Chem. Commun.*, 1981, 448.
8 R. D. Gillard, First International Conference on the Chemistry of the Platinum Group Metals, Bristol, July 1981, Lecture A8.
9 P. B. Hitchcock, K. R. Seddon, J. E. Turp, Y. Z. Yousif, J. A. Zora, E. C. Constable, and O. Wernberg, *J. Chem. Soc., Dalton Trans.*, submitted for publication.
10 E. C. Constable, K. R. Seddon, and J. E. Turp, Second International Conference on the Chemistry of the Platinum Group Metals, Edinburgh, July 1984, Poster D40.
11 E. C. Constable and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 1982, 34.
12 A. A. Grinberg, Kh. I. Gil'dengershel', and V. F. Budanova, *Russ. J. Inorg. Chem.*, 1966, **11**, 1351.
13 S. G. Hedin, *Acta Univ. Lund., Sect. 2*, 1886, **22**, 1.
14 J. W. Bunting, *Adv. Heterocycl. Chem.*, 1979, **25**, 1; ref. 69 of ref. 3.
15 O. Mønsted and G. Nord, *J. Chem. Soc., Dalton Trans.*, 1981, 2599.
16 R. D. Gillard and R. J. Wademan, *J. Chem. Soc., Dalton Trans.*, 1981, 2599.
17 R. D. Gillard and R. Ugo, *J. Chem. Soc. A*, 1966, 549.
18 O. Wernberg, unpublished work.
19 A. Albert and W. L. F. Armarego, *Adv. Heterocycl. Chem.*, 1965, **4**, 1.

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