Notes

Aqueous Chemistry of Platinum and Palladium Complexes. Synthesis and Crystal Structure of a Palladium(II) Aqua Complex with a Cyclometallated Ligand: $[PdL(H_2O)(ONO_2)]ClO_4 \cdot H_2O$ (L = 1-methyl-2,2'-bipyridin-3-ylium)‡

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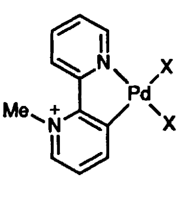
Treatment of $[Pd(L)Cl_2]$ **1** (L = 1-methyl-2,2'-bipyridin-3-ylium) with $AgNO_3$ in water yields $[PdL(H_2O)_2]^{2+}$ and NO_3^- which on evaporation to dryness affords $[PdL(ONO_2)_2]$ **2**. Addition of $NaClO_4$ to a solution of $[PdL(H_2O)_2]^{2+}$ gives crystals of $[PdL(H_2O)(ONO_2)]ClO_4 \cdot H_2O$ **3**. Crystals of **3** are monoclinic, space group *C*2/*c* with a = 19.383(8), b = 11.813(5), c = 13.636(5) Å, β = 95.55(2)° and Z = 8. Refinement of 3604 reflections [$I > 4\sigma(I)$] out of a total of 4460 reflections ($3 < 2\theta < 64°$) gave R and R' values of 0.040 and 0.042 respectively. The nitrato group is *trans* to the pyridyl nitrogen atom of L with a Pd–O distance of 2.052(3) Å. The Pd–OH_2 distance is 2.132(3) Å, consistent with the higher *trans* influence of the carbon-bonded *N*-methylpyridyl moiety.

Although aqua complexes of platinum(II) and palladium(II) exist in solution, the number of well characterized crystalline platinum(II) compounds with an aqua ligand is limited.[1,2] Crystal structures of palladium(II) complexes with an aqua ligand are even rarer than for platinum(II), probably as a result of its higher reactivity. To our knowledge, the only example is $[Pd(dmp)(bquin)(OH_2)]ClO_4$.[§,3]

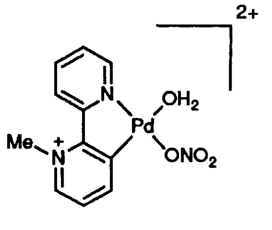
We describe herein some aqueous chemistry of the palladium complex of the ligand 1-methyl-2,2'-bipyridin-3-ylium (L). As a ligand L is isoelectronic with 2-phenylpyridine, which readily forms cyclometallated complexes. However, L is neutral overall, acts as a zwitterion, and thus gives the monomeric complexes $[M(L)Cl_2]$ (M = Pd or Pt).[4,5]

Experimental

Infrared spectra were recorded (4000–200 cm^{-1}) on a Perkin-Elmer 983 spectrophotometer using both Nujol and hexachlorobutadiene mulls (CsI plates) and caesium halide discs. Conductance measurements in water were measured at 25 °C with a Beckman RC-18A conductivity bridge. Carbon, H and N analyses were carried out by the Interuniversity Microanalytical Services, Ecole Nationale Supérieure de Chimie de Toulouse. The complex $[Pd(L)Cl_2]$ **1** was prepared by the method previously described.[4,5]



1, X = Cl
2, X = ONO_2



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Preparation of the Complexes.—**CAUTION**: perchlorate salts of metal complexes with organic ligands are potentially exposive and should be handled with the necessary precautions.[6]

$[PdL(ONO_2)_2]$ **2**. Silver nitrate (0.523 g, 3.07 mmol) was added to a stirred suspension of $[Pd(L)Cl_2]$ **1** (0.537 g, 1.54 mmol) in water (40 cm^3) whereupon AgCl precipitates immediately. The mixture was stirred for 10 min and the AgCl removed by centrifugation. A few drops of concentrated nitric acid were added to the pale yellow solution which was then evaporated to dryness. The compound was recrystallised from dilute nitric acid (pH ≈ 1), yield 65% (Found: C, 33.1; H, 2.5; N, 14.0. $C_{11}H_{10}N_4O_6Pd$ requires: C, 33.0; H, 2.5; N, 14.0%).

$[PdL(H_2O)(ONO_2)]ClO_4 \cdot H_2O$ **3**. Complex **2** (0.20 g, 0.50 mmol) was dissolved in the minimum amount of water to give a lemon-yellow solution. A concentrated solution of sodium perchlorate was added to the point of incipient turbidity. The solution was left for 3 d at ambient temperature whereupon yellow-orange cubes of **3** separated. The cubes (70%) were isolated, washed with water, ethanol and diethyl ether and dried *in vacuo* (Found: C, 27.7; H, 2.8; N, 8.8. $C_{11}H_{14}ClN_3O_9Pd$ requires: C, 27.9; H, 3.0; N, 8.9%). These cubes were used directly for the crystal-structure determination by X-ray diffraction.

X-Ray Crystal-structure Determination of $[PdL(H_2O)$-

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‡ Aqua(nitrato-κ*O*)(1-methyl-2,2'-bipyridin-3-ylium-κC^3,$N^{1'}$)palladium(II) perchlorate hydrate (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

§ Abbreviations used in this paper: L = 1-methyl-2,2'-bipyridin-3-ylium, dmp = 2-(dimethylaminomethyl)phenyl, bquin = benzo[*h*]quinoline, bipy = 2,2'-bipyridine, en = 1,2-diaminoethane and dien = diethylenetriamine.

Table 1 Positional parameters with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pd	0.413 08(1)	0.282 79(3)	0.386 31(2)
O(1)	0.335 1(2)	0.407 3(3)	0.401 0(2)
O(2)	0.338 3(2)	0.159 3(3)	0.378 7(2)
N(1)	0.490 4(2)	0.392 9(4)	0.380 3(2)
C(1)	0.489 1(2)	0.176 5(4)	0.378 3(3)
C(2)	0.482 3(2)	0.061 3(4)	0.375 9(3)
C(3)	0.540 8(3)	−0.005 6(5)	0.372 6(4)
C(4)	0.604 6(2)	0.045 1(5)	0.374 2(3)
N(2)	0.611 6(2)	0.159 3(4)	0.376 9(3)
C(5)	0.554 9(2)	0.227 0(4)	0.377 3(3)
C(6)	0.555 5(2)	0.350 3(4)	0.376 6(3)
C(7)	0.609 8(2)	0.426 3(5)	0.370 5(3)
C(8)	0.597 6(3)	0.542 4(5)	0.369 0(4)
C(9)	0.532 0(3)	0.581 3(5)	0.372 6(4)
C(10)	0.478 8(2)	0.504 6(4)	0.378 4(3)
C(11)	0.683 3(2)	0.204 6(6)	0.383 2(4)
N(3)	0.307 2(2)	0.146 1(4)	0.457 5(3)
O(3)	0.258 1(2)	0.079 4(3)	0.452 9(3)
O(4)	0.327 4(2)	0.198 5(3)	0.532 1(2)
Cl	0.361 79(6)	0.778 4(1)	0.339 28(9)
O(5)	0.362 7(3)	0.687 5(4)	0.407 4(3)
O(6)	0.334 7(3)	0.875 9(4)	0.382 7(4)
O(7)	0.312 6(3)	0.747 7(5)	0.257 3(4)
O(8)	0.425 3(3)	0.797 2(5)	0.303 8(6)
O(w)	0.745 3(2)	0.500 8(4)	0.240 4(3)

$(ONO_2)]ClO_4 \cdot H_2O$, 3.—*Crystal data.* $C_{11}H_{14}ClN_3O_9Pd$, $M = 474.10$, monoclinic, space group *C*2/*c* (no. 15), $a = 19.383(8)$, $b = 11.813(5)$, $c = 13.636(5)$ Å, $\beta = 95.55(2)°$, $U = 3107.5$ Å^3, $Z = 8$, $D_c = 1.64$ g cm^{-3}, $F(000) = 1888$, Mo-Kα radiation, $\lambda = 0.710\,73$ Å, $\mu = 11.3$ cm^{-1}.

Data collection. A colourless prismatic crystal of approximate dimensions $0.10 \times 0.20 \times 0.40$ mm was mounted on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal, incident beam monochromator. The unit-cell dimensions were determined at −105 °C in the range $8 < \theta < 11°$ with a take off angle of 3.5°. A data set of 4460 reflections was recorded by the θ–2θ technique (scan width $= 0.9 + 0.347 \tan\theta$, scan speed 1–10° nm^{-1}). The intensities of three standard reflections monitored every hour showed no significant variation during the data collection. After rejection of systematic absences (h, 0, $l = 2n$) 3604 reflections having intensities greater than 4.0 times their standard deviations were used in the structure determination. Lorentz and polarisation corrections were applied to the data (relative transmission coefficients 0.815–1.00, average value 0.947).

Structure determination. The structure was solved by the heavy-atom method. The space group *C*2/*c*, consistent with the extinctions, was chosen. After location of the Pd atom by a Patterson map, subsequent full-matrix least-squares refinement and interpretation of a Fourier difference map enabled all the non-hydrogen atoms to be located; these were refined anisotropically. Hydrogen atoms were located on a Fourier difference map, and added to the structure factor calculations, but their positions were not refined.

Neutral atom scattering factors were used.[7] Anomalous dispersion effects were included in F_c;[8] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer and Waber.[9] Weights, $w = 1$ of all observed reflections, were applied and gave satisfactory weight analyses. The final cycle of refinement included 226 variable parameters and converged with $R = \Sigma\{|F_o| - |F_c|\}/\Sigma|F_o| = 0.040$ and $R' = [\Sigma w(F_o - F_c)^2/\Sigma F_o{}^2]^{\frac{1}{2}} = 0.042$. A final Fourier difference map showed no electron density greater than 0.54 e Å^{-3}. All calculations were performed on a VAX 11/730 Digital computer using the Enraf-Nonius SDP software package.[10] Atomic coordinates are listed in Table 1.

Additional data available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Complex $[PdL(ONO_2)_2]$ **2** was prepared by the reaction of $[Pd(L)Cl_2]$ **1** with silver nitrate in water. The presence of co-ordinated nitrate was confirmed by IR spectroscopy (point group C_{2v} for covalent nitrate).[11–13] The spectrum of **2** as a mull shows considerable splitting of the ν_2 band (N–O stretch) which is larger than that observed for $[Pd(bipy)(ONO_2)_2]$.[14] This can be attributed to the unsymmetrical nature of L since the σ-bonded carbon has a higher *trans* influence compared with a nitrogen atom.

For nitrato complexes the Pd–O stretching modes are in the same region as Pd–Cl stretching modes. The band at 339 cm^{-1} in the IR spectrum of **2** is identified as a ν(Pd–O) mode. The other band cannot be identified with certainty as there are a number of strong absorptions in the region 330–230 cm^{-1}. The IR spectrum of **2** as a caesium halide disc corresponds to that for $[Pd(L)X_2]$ (X = Cl or Br) plus strong bands at 1360 and 834 cm^{-1} due to ionic nitrate.

Dissolution of a nitrato complex in water results in the complete aquation of the nitrato ligand as has been shown by Raman spectroscopy.[15] The molar conductivity of **2** in water is 247 S cm^2 mol^{-1} (1×10^{-3} mol dm^{-3}), which is typical of a 2:1 electrolyte, indicating that the hydrolysis in equation (1) is

$$[PdL(ONO_2)_2] \xrightarrow{H_2O} [PdL(H_2O)_2]^{2+} + 2NO_3^- \quad (1)$$

complete and that the resultant diaqua complex is not noticably acidic. The conductance of *cis*-$[Pt(NH_3)_2(H_2O)_2][NO_3]_2$, which has p$K_a$ values of 5.6 and 7.3, is 264 S cm^2 mol^{-1} (1×10^{-3} mol dm^{-3}).[15a] In contrast, the molar conductivity of $[Pd(bipy)(ONO_2)_2]$ in water is 320 S cm^2 mol^{-1}. We have shown previously[14] that this complex, on dissolution in water, rapidly forms the dihydroxy-bridged dimer, $[Pd(bipy)(\mu\text{-}OH)]_2{}^{2+}$ [equation (2)]; hence, the higher molar conductance

$$[Pd(bipy)(ONO_2)_2] \xrightarrow{H_2O} 0.5\,[Pd(bipy)(\mu\text{-}OH)]_2{}^{2+} + H^+ + 2NO_3{}^- \quad (2)$$

is due to the nitric acid formed concomitantly.

When a solution of **2** in water containing sodium perchlorate is allowed to stand for several hours at room temperature, bright yellow crystals of $[PdL(H_2O)(ONO_2)]ClO_4 \cdot H_2O$ **3** separate. The IR spectrum of **3**, apart from water and perchlorate bands, is essentially similar to that of **2**, except that the band due to ν_2 of the co-ordinated nitrate at 1012 cm^{-2} is no longer split. The Pd–ONO$_2$ stretching mode is assigned to the band at 340 cm^{-1}. The Pd–OH$_2$ mode cannot be identified.

Structure of $[PdL(H_2O)(ONO_2)]ClO_4 \cdot H_2O$ **3**.—The interatomic distances and bond angles are given in Table 2 and the structure is shown in Fig. 1. The structure consists of a $[PdL(H_2O)(ONO_2)]^+$ cation, perchlorate anion and one molecule of water of crystallisation in each asymetric unit. The co-ordination about palladium is essentially planar with a slight tetrahedral distortion. The deviations from the weighted best plane is no more than 0.067(4) Å.

The ligand L is expected to resemble both bipy and 2-phenylpyridine. The Pd–N(1) bond distance is 1.993(4) Å which compares with 2.034(1) Å (mean value) for $[Pd(bipy)_2][NO_3]_2 \cdot H_2O$[16] and 2.02 Å for $(\{\overline{Pd[C_6H_3(NO_2\text{-}4)(C_5H_4N}\text{-}2)](\mu\text{-}O_2CMe)\}_2)$.[17] The Pd–C(1) bond distance is 1.946(4) Å which compares with 1.94(1) Å for $(\{\overline{Pd[C_6H_3(NO_2\text{-}4)(C_5H_4N}\text{-}2)](\mu\text{-}O_2CMe)\}_2)$,[17] 1.981(6) Å for $[NEt_4][Pd\{C_6H_4C(Me){=}$

Table 2 Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Pd–O(1)	2.132(3)	Pd–N(1)	1.993(4)
Pd–O(2)	2.052(3)	Pd–C(1)	1.946(4)
O(1)–Pd–O(2)	89.5(1)	O(2)–Pd–N(1)	173.1(1)
O(1)–Pd–N(1)	95.5(1)	O(2)–Pd–C(1)	94.2(2)
O(1)–Pd–C(1)	175.8(1)	N(1)–Pd–C(1)	80.9(2)
C(1)–C(2)	1.368(7)	C(5)–C(6)	1.457(7)
C(2)–C(3)	1.386(7)	C(6)–C(7)	1.392(7)
C(3)–C(4)	1.373(8)	C(7)–C(8)	1.391(8)
C(4)–N(2)	1.356(7)	C(8)–C(9)	1.358(7)
N(2)–C(11)	1.483(6)	C(9)–C(10)	1.382(7)
N(2)–C(5)	1.361(6)	N(1)–C(10)	1.338(7)
C(1)–C(5)	1.409(6)	N(1)–C(6)	1.364(5)
C(1)–C(2)–C(3)	119.5(4)	N(2)–C(5)–C(6)	125.5(4)
C(2)–C(3)–C(4)	119.3(6)	N(1)–C(6)–C(5)	111.1(4)
C(3)–C(4)–N(2)	121.5(5)	N(1)–C(6)–C(7)	118.1(4)
C(4)–N(2)–C(5)	120.4(4)	C(5)–C(6)–C(7)	130.7(4)
C(4)–N(2)–C(11)	116.9(5)	C(6)–C(7)–C(8)	120.6(4)
C(5)–N(2)–C(11)	122.7(4)	C(7)–C(8)–C(9)	119.4(5)
C(1)–C(5)–N(2)	119.0(4)	C(8)–C(9)–C(10)	119.1(5)
C(2)–C(1)–C(5)	120.3(4)	N(1)–C(10)–C(9)	121.5(4)
C(1)–C(5)–C(6)	115.5(4)	C(6)–N(1)–C(10)	121.2(4)
O(2)–N(3)	1.290(5)	N(3)–O(3)	1.233(5)
N(3)–O(4)	1.223(6)		
O(2)–N(3)–O(3)	117.0(4)	O(2)–N(3)–O(4)	119.6(4)
O(3)–N(3)–O(4)	123.3(4)		

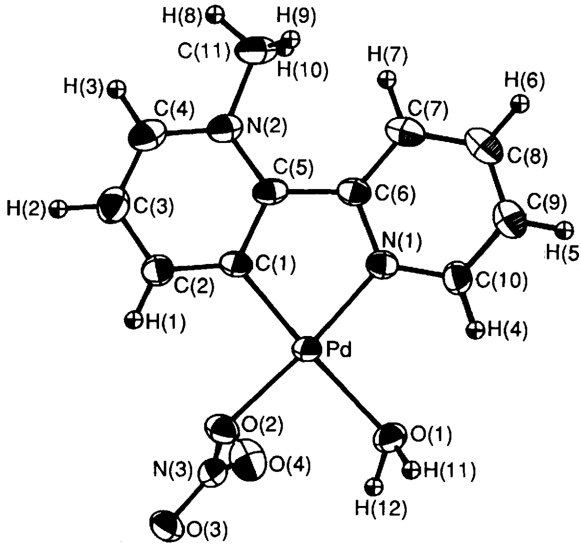

Fig. 1 ORTEP diagram of the $[PdL(H_2O)(ONO_2)]^+$ cation showing the atomic numbering scheme

NNHPh}ClBr][18] and 1.94(1) Å for $[Pd(dmp)(bquin)(H_2O)]ClO_4$.[3]

The bite of the ligand L gives a N(1)–Pd–C(1) angle of 80.9(2)° which compares with 80.0° for $[Pd(bipy)_2][NO_3]_2$,[16] 80(1)° for $[Pt(bipy)Cl_2]$,[19] 80.1° for $[Pt(bipy)_2]^{2+}$ [20] and 81.4(2)° for $(\{Pd[C_6H_3(NO_2\text{-}4)(C_5H_4N\text{-}2)](\mu\text{-}O_2CMe)\}_2)$.[17] The small bite of L results in a N(1)–C(6)–C(5) angle of 111.1(4)° and a C(1)–C(5)–C(6) angle of 115.5(4)°. Both the pyridyl ring and the cyclometallated *N*-methylpyridyl ring are planar with a dihedral angle of 3.9°. The steric interactions between the C(11) methyl group and the hydrogen of C(7) are relieved by a deviation of C(11) out of the plane of the ring by 0.091 Å and to a lesser extent by a C(5)–N(2)–C(11) angle of 122.7(4)°. The dihedral angle between the plane of the complex and the pyridyl ring is 5.2° while the same angle for the cyclometallated ring is 3.2°. The slight tetrahedral distortion about the palladium is probably due to this twisting of the ligand. The corresponding dihedral angles in $(\{Pd[C_6H_3(NO_2\text{-}4)(C_5H_4N\text{-}2)](\mu\text{-}O_2CMe)\}_2)$ are 3.7 and 4.6°, suggesting that for L the C(11) methyl group has a minor steric effect.

The nitrate ion is *trans* to the pyridyl nitrogen atom. The Pd–O(2) bond distance is 2.052(3) Å. The N(3)–O(2) bond [1.290(5) Å] is lengthened relative to N(3)–O(3) [1.233(5) Å] and N(3)–O(4) [1.223(6) Å]. The dihedral angle between the mean nitrate plane and the basal palladium plane is 68.9 ± 0.15° resulting in a Pd ··· O(4) distance of 2.89 Å, which indicates essentially a monodentate nitrate group. A lengthening of the N–O bond has been observed in *cis*-$[Pt(NH_3)_2(ONO_2)_2]$[15a] and $[Pd(dien)(ONO_2)]NO_3$.[15b]

The Pd–O(1) bond distance is 2.132(3) Å, which suggests a rather long bond. However, this and the Pd–O(2) distance seem to be typical Pd–O bond lengths. In $(\{Pd[C_6H_3(NO_2\text{-}4)(C_5H_4N\text{-}2)](\mu\text{-}O_2CMe)\}_2)$ the Pd–O bond distance *trans* to the pyridyl N is 2.03(1) Å while that *trans* to the phenyl C is lengthened to 2.14(2) Å. To our knowledge the only other well characterised palladium aqua complex is $[Pd(dmp)(bquin)(H_2O)]ClO_4$ with a Pd–O distance of 2.20(1) Å. The aqua ligand is *trans* to the phenyl of dmp.[3]

The chlorine atom of the perchlorate anion is linked to the oxygen atoms O(5), O(6), O(7) and O(8). The crystal packing is stabilised by hydrogen bonds, the centre of which is the water molecule O(w) with its two hydrogens H(13) and H(14).

The acidity of co-ordinated water molecules depends on the nature of the other ligands present on the metal. The aqua–hydroxo complex formed as a result of hydrolysis can dimerise *via* hydroxo bridges. Thus, $[Pd(en)(H_2O)_2]^{2+}$ is stable in acidic solution and dimerises only during titration with NaOH,[21] whereas $[Pd(bipy)(H_2O)_2]^{2+}$ is more acidic and the dimer $[Pd(bipy)(\mu\text{-}OH)_2(bipy)Pd]^{2+}$ is the only complex present even in acidic solutions.[14] Altering one of the donor atoms on bipy from nitrogen to carbon has a marked effect on the acidic properties of the aqua complex.

References

1 J. F. Britten, B. Lippert, C. J. L. Lock and P. Pilon, *Inorg. Chem.*, 1982, **21**, 1936.

2 F. D. Rochon and R. Melanson, *Inorg. Chem.*, 1987, **26**, 989.

3 A. J. Deeming, I. P. Rothwell, M. B. Hursthouse and L. New, *J. Chem. Soc., Dalton Trans.*, 1978, 1490.

4 S. Dholakia, F. L. Wimmer and R. D. Gillard, *Inorg. Chim. Acta*, 1983, **69**, 179.

5 S. Wimmer and F. L. Wimmer, *Polyhedron*, 1985, **4**, 1665.

6 K. N. Raymond, *Chem. Eng. News*, 1983, **61**, 4; W. C. Wolsey, *J. Chem. Educ.*, 1973, **50**, A335.

7 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2B.

8 J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 1964, **17**, 781.

9 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, vol. 4, Table 2.3.1.

10 B. A. Frenz, 'The Enraf-Nonius CAD 4 SDP. A Real Time System for Concurrent X-Ray Data Collection and Crystal Structure Determination,' in *Computing in Crystallography*, eds. H. Schenk, R. Olthof-Mazekamp, H. Vankoningsveld and G. C. Bassi, Delft University Press, Holland, 1978, p. 64.

11 B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Chem. Soc.*, 1957, 4222.

12 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley Interscience, New York, 4th edn., 1986; U. Casellato, P. A. Vigato and M. Vidali, *Coord. Chem. Rev.*, 1981, **36**, 183; C. C. Addison and D. Sutton, *Prog. Inorg. Chem.*, 1967, **8**, 195.

13 C. C. Addison and B. M. Gatehouse, *J. Chem. Soc.*, 1960, 613.

14 S. Wimmer, F. L. Wimmer, P. Castan and N. P. Johnson, *J. Chem. Soc., Dalton Trans.*, 1989, 403.
15 (*a*) B. Lippert, C. J. L. Lock, B. Rosenberg and M. Zvagulis, *Inorg. Chem.*, 1977, **16**, 1525; (*b*) J. F. Britten, C. J. L. Lock and W. M. C. Pratt, *Acta Crystallogr., Sect. B*, 1982, **38**, 2148.
16 P. C. Chieh, *J. Chem. Soc., Dalton Trans.*, 1972, 1643.
17 J. Selbin, K. Abboud, S. F. Watkins, M. A. Gutierrez and F. R. Fronczek, *J. Organomet. Chem.*, 1983, **241**, 259.
18 J. Dehand, J. Fischer, M. Pfeffer, A. Mitschler and M. Zinsius, *Inorg. Chem.*, 1976, **15**, 2675.
19 R. S. Osborn and D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1974, 1002.
20 A. Hazell, O. Simonson and O. Wernberg, *Acta Crystallogr., Sect. C*, 1986, **42**, 1707.
21 M. C. Lim and R. B. Martin, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1911.

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