and as seen from the view in Figure 1 has a pseudo-2-fold axis passing through the C(22) and C(32) bond and Pt(1). The metrical details (in the form minimum, maximum, and mean) of the coordination about Pt are the Pt–N distance of 2.03 (1), 2.09 (1), and 2.06 (2) Å, the bite angle about Pt of the five-membered rings of 84.1 (6), 86.3 (5), and 85 (1)°, the bite angle about Pt of the six-membered rings of 86.5 (5), 94.3 (5), and 91 (3)°, and the angle of the trans nitrogen atoms of 172.1 (4), 174.9 (6), and 173 (1)°. The variation in these quantities indicates large deviations from octahedral geometry, although the twist angle between the two triangular faces of cation Pt(2) necessarily is 60°, corresponding to octahedral geometry, whereas the average of that of cation Pt(1) is 52°. These indicate a considerable difference from the near-trigonal-prismatic value of 16° for $[Pt(sep)]^{4+}$.[2] Two of the ethane bridging groups of cation Pt(1) adopt an "*ob*" configuration and the other "*lel*", whereas all three of cation Pt(2) are of the "*lel*" form.

Initially, there was no reason to suspect that the product from the $SnCl_2/HCl$ reduction of $[Pt((NO_2)_2sar)]^{3+}$ was anything but $[Pt((NH_2)_2sar)]^{4+}$, as the ^1H and ^{13}C NMR spectra and the microanalytical data[1] were all consistent with this formulation. For instance, the ^1H NMR and UV/vis spectra do not allow the complexes $[Co((NH_2)_2sar)]^{3+}$ and $[Co((NHOH)_2sar)]^{3+}$ to be distinguished,[4,13] so it is also expected that they will be similar for the Pt analogue. Further, the microanalytical data for both the Cl^- and $CF_3SO_3^-$ salts[1] are equally consistent with a hydrated form of $[Pt((NH_2)_2sar)]^{4+}$ or $[Pt((NHOH)_2sar)]^{4+}$. The first indication that the supposed "$[Pt((NH_2)_2sar)]^{4+}$" complex was not the major product of the $SnCl_2/HCl$ reduction of $[Pt((NO_2)_2sar\text{-}H)]^{3+}$ arose from the study of the $SnCl_2/HCl$ reductions of $[Co((NO_2)_2sar)]^{3+}$, where the major product is $[Co((NHOH)_2sar)]^{3+}$.[4] This in turn led to a reexamination of the ^1H-decoupled ^{13}C NMR spectrum[1] of "$[Pt((NH_2)_2sar)]^{4+}$", which indicated that the chemical shift of the quaternary carbons was more in keeping with those bound to hydroxylamine substituents rather than amine substituents.[4,5]

The interpretation of the electrochemical experiments reported in the initial paper[1] are not affected by the present result, as the complexes $[Pt((NH_2)_2sar)]^{4+}$ and $[Pt((NHOH)_2sar)]^{4+}$ are expected to have identical reduction potentials, by analogy with their cobalt counterparts.[14] Moreover, the hydroxylamine substituent is not electroactive under the conditions reported in the original paper;[1] thus, the transient reduction product of the pulse radiolysis and electrochemical experiments is not due to a hydroxylamine radical anion but to the Pt(III) complex $[Pt^{III}(NHOH)_2sar]^{3+}$.

The X-ray data on $[Pt((NHOH)_2sar)](CF_3SO_3)_4{\cdot}H_2O$ also throw light on the ESR spectra of the Pt(III) complexes observed in the γ-radiolysis of solid samples of this complex and the analogous chloride salt.[1] It was expected that these Pt(III) complexes should give rise to a central peak due to the isotopes ^{190}Pt, ^{192}Pt, ^{194}Pt, ^{196}Pt, and ^{198}Pt with a doublet centered about this peak due to the ^{195}Pt ($I = {}^1/_2$) isotope. While this was observed for the chloride salt, the spectrum due to the Pt(III) trapped in $[Pt((NHOH)_2sar)](CF_3SO_3)_4$ is more complex and looks more like two overlapping Pt(III) signals of equal intensity. The presence of two structurally distinct Pt(IV) ions in the $[Pt((NHOH)_2sar)](CF_3SO_3)_4{\cdot}H_2O$ lattice resolves this apparent discrepancy.

It is also clear that the observed ESR signals are not due to reduction of the hydroxylamine substituents, because of the appreciable ^{195}Pt hyperfine splitting of the signals (~60 G) and the prolonged life of these paramagnetic species. The irradiated solid samples could be kept for weeks at room temperature and in the presence of O_2 in the solid state without any noticeable deterioration of the signal.

Acknowledgment. We are grateful to Dr. W. T. Robinson and the University of Canterbury, Christchurch, New Zealand, for use of X-ray diffraction facilities, and to the ANU Microanalytical Service.

Registry No. $[Pt((NHOH)_2sar)](CF_3SO_3)_4{\cdot}H_2O$, 115731-60-7.

Supplementary Material Available: For $[Pt((NHOH)_2sar)](CF_3SO_3){\cdot}H_2O$, tables of positional parameters, thermal parameters, and bond distances and angles and a full labeling scheme for cations Pt(1) and Pt(2) (13 pages); listings of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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(13) The protons due to the $-NH_2$ and $-NHOH$ substituents are not observed in D_2O solutions because of rapid exchange.

(14) Bond, A. M.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 2010.

Contribution from the Departments of Chemistry,
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Ruthenium Carbonyl Complexes of 2,4,6-Tris(2-pyridyl)-1,3,5-triazine. Crystal Structure of Methoxide-Substituted [μ-2,4,6-Tris(2-pyridyl)-1,3,5-triazine]bis[dicarbonyldichlororuthenium(II)]

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and Arnold L. Rheingold‡

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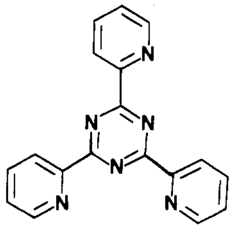
The ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPT) has been studied extensively as an analytical reagent for various metals.[1-3] It functions primarily as a tridentate ligand, similar to 2,2′:6′,2″-terpyridine(tpy), forming complexes of the general type $[M(TPT)_2]^{2+}$ (M = Ru,[1] Co,[2,3] Fe[4,5]), $M(TPT)(NO_3)_3$ (M = lanthanide[6]), or $M(TPT)Cl_2$ (M = Co,[3] Sc,[7] Fe or Zn[8]). The coordination of a second metal to TPT is not usually observed due to deactivation of the triazine ring by the inductive effect of the first metal and as a result of steric interaction between the hydrogen atoms and the metal ion.[6] Further work has indicated that TPT is a more versatile ligand than tpy and that it may function simultaneously as a tridentate and bidentate ligand in dicobalt[3] and dimercury[9] complexes. Only a few TPT complexes have been examined crystallographically.[10]



TPT

Our continuing interest[11] in reactions of N-donor heterocyclic molecules with polymeric dicarbonyldichlororuthenium(II), $[Ru(CO)_2Cl_2]_n$, led to the reaction of this complex with TPT in methanol. In the absence of light, the bimetallic complex $(\mu\text{-}TPT)[Ru(CO)_2Cl_2]_2$ has been obtained from this reaction. By contrast, a similar reaction in the presence of visible light yields $\{\mu\text{-}C_3N_3(OMe)(py)_2(pyH)\}[Ru(CO)_2Cl_2]_2$, formed by photochemically activated nucleophilic attack by methanol at the triazine ring. X-ray crystallographic and spectroscopic data for the complex are reported.

Experimental Section

2,4,6-Tris(2-pyridyl)-1,3,5-triazine and methanol (HPLC grade) were obtained from Aldrich and used without further purification. Polymeric dicarbonyldichlororuthenium(II) was prepared according to the reported method.[12] Microanalyses were obtained by Galbraith Laboratories, Knoxville, TN. Infrared spectra were recorded as Nujol mulls between

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Table I. Crystallographic Data for $\{\mu\text{-}C_3N_3(OMe)(py)(pyH)\}[Ru(CO)_2Cl_2]_2\cdot MeOH$

formula: $C_{24}H_{20}Cl_4N_6O_6Ru_2$	fw: 832.4
a = 9.297 (4) Å	space group: $P\bar{1}$
b = 11.477 (3) Å	T = 23 °C
c = 15.945 (7) Å	λ = 0.71073 Å
α = 85.77 (3)°	ρ_{calcd} = 1.71 g cm^{-3}
β = 73.62 (3)°	μ = 12.9 cm^{-1}
γ = 86.20 (3)°	R_F = 4.67%
V = 1610 (1) Å^3	R_{wF} = 5.41%
Z = 2	

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)

	x	y	z	U^a
Ru(1)	8327.2 (4)	217.8 (4)	1958.2 (3)	42.6 (2)
Ru(2)	2940.6 (5)	4258.3 (4)	3013.8 (3)	51.1 (2)
Cl(1)	7134 (2)	−398 (1)	929 (1)	63 (1)
Cl(2)	9408 (2)	625 (1)	3110 (1)	59 (1)
Cl(3)	3707 (2)	4840 (1)	4235 (1)	64 (1)
Cl(4)	1930 (2)	3612 (2)	1914 (1)	92 (1)
N(1)	7228 (5)	−1101 (4)	2862 (3)	44 (1)
N(2)	6240 (4)	1101 (3)	2642 (3)	38 (1)
N(3)	4091 (5)	807 (4)	3878 (3)	46 (1)
N(4)	4198 (4)	2622 (3)	3032 (3)	40 (1)
N(5)	1385 (5)	3221 (4)	3960 (3)	52 (2)
N(6)	4572 (5)	1668 (4)	1354 (3)	52 (2)
O(1)	11020 (5)	−1303 (5)	1061 (3)	89 (2)
O(2)	9858 (5)	2233 (5)	791 (3)	88 (2)
O(3)	5343 (8)	5702 (5)	1797 (4)	117 (3)
O(4)	904 (7)	6406 (5)	3071 (4)	110 (3)
O(5)	6763 (4)	3104 (3)	2425 (3)	51 (1)
O(6)^b	2808 (5)	47 (5)	2314 (4)	93 (2)
C(16)^b	3148 (9)	−1166 (9)	2427 (6)	96 (4)
C(1)	7683 (7)	−2237 (5)	2937 (4)	64 (2)
C(2)	6963 (8)	−2994 (5)	3602 (5)	71 (3)
C(3)	5729 (7)	−2595 (5)	4242 (4)	59 (2)
C(4)	5231 (6)	−1450 (4)	4177 (4)	49 (2)
C(5)	5982 (5)	−723 (4)	3481 (3)	40 (2)
C(6)	5426 (5)	495 (4)	3332 (3)	38 (2)
C(7)	3557 (6)	1876 (4)	3679 (3)	41 (2)
C(8)	5684 (5)	2289 (4)	2451 (3)	39 (2)
C(9)	1982 (6)	2183 (5)	4205 (4)	46 (2)
C(10)	1183 (6)	1450 (5)	4862 (4)	57 (2)
C(11)	−339 (7)	1777 (6)	5281 (4)	74 (3)
C(12)	−954 (7)	2794 (6)	5032 (4)	74 (3)
C(13)	−73 (7)	3511 (6)	4379 (5)	67 (3)
C(20)	10016 (6)	−717 (6)	1403 (4)	59 (2)
C(21)	9251 (6)	1484 (5)	1229 (4)	55 (2)
C(22)	4460 (9)	5128 (6)	2234 (5)	77 (3)
C(23)	1646 (8)	5592 (6)	3051 (4)	70 (3)
C(24)	7132 (8)	3203 (5)	3230 (5)	64 (3)
C(25)	4286 (8)	1682 (6)	555 (4)	69 (3)
C(26)	5018 (10)	2419 (7)	−109 (5)	85 (3)
C(27)	6053 (9)	3156 (7)	10 (4)	86 (3)
C(28)	6322 (8)	3136 (6)	842 (4)	67 (3)
C(29)	5545 (6)	2390 (5)	1515 (4)	46 (2)

^{a}Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^{b}Atoms from solvent of crystallization.

Table III. Selected Bond Lengths (Å) and Angles (deg)

(a) Bond Lengths			
Ru(1)–Cl(1)	2.386 (2)	N(2)–C(6)	1.321 (6)
Ru(1)–Cl(2)	2.408 (2)	N(2)–C(8)	1.466 (6)
Ru(1)–N(1)	2.110 (4)	N(3)–C(6)	1.335 (6)
Ru(1)–N(2)	2.152 (4)	N(3)–C(7)	1.341 (6)
Ru(1)–C(20)	1.869 (6)	N(4)–C(7)	1.319 (6)
Ru(1)–C(21)	1.883 (6)	N(4)–C(8)	1.464 (6)
Ru(2)–Cl(3)	2.400 (2)	O(5)–C(8)	1.399 (6)
Ru(2)–Cl(4)	2.387 (3)	O(5)–C(24)	1.431 (9)
Ru(2)–N(4)	2.143 (4)	C(5)–C(6)	1.483 (7)
Ru(2)–N(5)	2.118 (4)	C(7)–C(9)	1.490 (7)
Ru(2)–C(22)	1.876 (7)	C(8)–C(29)	1.529 (8)
Ru(2)–C(23)	1.870 (7)		
(b) Bond Angles			
Cl(1)–Ru(1)–Cl(2)	172.8 (1)	Cl(4)–Ru(2)–N(5)	88.9 (2)
Cl(1)–Ru(1)–N(1)	88.8 (1)	N(4)–Ru(2)–N(5)	77.6 (2)
Cl(2)–Ru(1)–N(1)	84.1 (1)	Cl(3)–Ru(2)–C(22)	90.7 (3)
Cl(1)–Ru(1)–N(2)	90.1 (1)	Cl(4)–Ru(2)–C(22)	95.4 (3)
Cl(2)–Ru(1)–N(2)	89.4 (1)	N(4)–Ru(2)–C(22)	98.7 (2)
N(1)–Ru(1)–N(2)	77.3 (1)	N(5)–Ru(2)–C(22)	174.4 (3)
Cl(1)–Ru(1)–C(20)	87.0 (2)	Cl(3)–Ru(2)–C(23)	91.3 (3)
Cl(2)–Ru(1)–C(20)	92.8 (2)	Cl(4)–Ru(2)–C(23)	87.4 (3)
N(1)–Ru(1)–C(20)	96.4 (2)	N(4)–Ru(2)–C(23)	173.5 (2)
N(2)–Ru(1)–C(20)	173.1 (2)	N(5)–Ru(2)–C(23)	96.4 (2)
Cl(1)–Ru(1)–C(21)	94.4 (2)	C(22)–Ru(2)–C(23)	87.5 (3)
Cl(2)–Ru(1)–C(21)	92.7 (2)	Ru(1)–N(2)–C(6)	114.4 (3)
N(1)–Ru(1)–C(21)	175.1 (2)	Ru(1)–N(2)–C(8)	127.5 (3)
N(2)–Ru(1)–C(21)	99.0 (2)	C(6)–N(2)–C(8)	118.1 (4)
C(20)–Ru(1)–C(21)	87.4 (3)	C(6)–N(3)–C(7)	113.5 (4)
Cl(3)–Ru(2)–Cl(4)	173.7 (1)	Ru(2)–N(4)–C(7)	114.0 (3)
Cl(3)–Ru(2)–N(4)	90.5 (1)	Ru(2)–N(4)–C(8)	127.5 (3)
Cl(4)–Ru(2)–N(4)	90.1 (1)	C(7)–N(4)–C(8)	118.4 (4)
Cl(3)–Ru(2)–N(5)	85.2 (2)	C(8)–O(5)–C(24)	115.5 (4)

KBr plates with a Perkin-Elmer 167 instrument. A Bruker AM 400 spectrometer was used for ^{1}H NMR measurements, and DMSO-d_6 was employed as the solvent. Electronic spectra were obtained in methanol with a Perkin-Elmer Lambda 3A spectrophotometer. The fast atom bombardment mass spectrum was obtained with a VG70E spectrometer. Xenon was used as the bombarding gas. The operating pressure of the ion source was 2 × 10^{-5} Torr, and the ions were accelerated at 4 kV.

Preparation of $(\mu\text{-TPT})[Ru(CO)_2Cl_2]_2\cdot{}^1/_2CH_3COCH_3$. The following reaction was carried out in the dark. A mixture of $[Ru(CO)_2Cl_2]_n$ (0.15 g, 0.66 mmol) and methanol (25 mL) was refluxed for 10 min and filtered into a solution of TPT (0.10 g, 0.32 mmol) in methanol (15 mL). The resulting solution was refluxed for 10 min and allowed to cool to room temperature. When this mixture stood for several hours, a yellow solid precipitated, which was collected and recrystallized from acetone; yield 0.21 g (53%). Anal. Calcd for $C_{22}H_{12}Cl_4N_6O_4Ru_2\cdot{}^1/_2C_3H_6O$: C, 35.40; H, 1.90; N, 10.5. Found: C, 35.32; H, 2.40; N, 9.74. IR: 2050 vs, 1993 vs, 1698 m cm^{-1}. ^{1}H NMR: δ 9.06 (d, $H_{6,6'}$), 8.86 (d, $H_{3,3'}$), 8.49 (m, $H_{5''}$), 8.35 (m, $H_{3'',4,4',4''}$), 7.87 (dd, $H_{5,5'}$), 7.62 (m, $H_{6''}$), 2.51 (s, CH_3). Visible spectrum (λ_{max} (ε)): 419 (5.05 × 10^3) nm.

Preparation of $\{\mu\text{-}C_3N_3(OMe)(py)_2(pyH)\}[Ru(CO)_2Cl_2]_2\cdot MeOH$. The above reaction was repeated in the presence of ordinary laboratory lighting. After the reaction mixture stood at room temperature for several hours, large, dark-colored crystals were filtered off; yield 65%. Anal. Calcd for $C_{24}H_{20}Cl_4N_6O_6Ru_2$: C, 34.63; H, 2.42; N, 10.1. Found: C, 34.68; H, 2.82; N, 9.80. IR: 3375 w, br, 2052 vs, 1980 vs, 1259 m cm^{-1}. ^{1}H NMR: δ 9.10 (d, $H_{6,6'}$), 8.93 (d, $H_{3,3'}$), 8.59 (dd, $H_{5''}$), 8.51 (br s, pyH$^+$), 8.36 (m, $H_{3'',4,4',4''}$), 7.88 (m, $H_{6'',5,5'}$), 3.83 (s, CH_3). Visible spectrum (λ_{max} (ε)): 423 (5.00 × 10^3) nm. Mass spectrum: *m/e* 801 (20%), 770 (36%), 735 (45%), 707 (27%), 672 (28%), 644 (34%).

Structure Determination

A crystal of $C_{23}H_{16}Cl_4N_6O_5Ru_2\cdot CH_3OH$ (II) was attached to a fine glass fiber with epoxy cement. The compound crystallizes in the triclinic space group $P\bar{1}$ with Z = 2. The centrosymmetric alternative was initially assumed and later confirmed by the chemically sensible and com-

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(1) Embry, W. A.; Ayres, G. H. *Anal. Chem.* **1968**, *40*, 1499.

(2) Janmohamed, M. J.; Ayres, G. H. *Anal. Chem.* **1972**, *44*, 2263.

(3) Vagg, R. S.; Warrener, R. N.; Watton, E. C. *Aust. J. Chem.* **1969**, *22*, 141.

(4) Pagenkoft, G. K.; Margerum, D. W. *Inorg. Chem.* **1968**, *7*, 2514.

(5) Collins, P.; Diehl, H.; Smith, G. F. *Anal. Chem.* **1959**, *31*, 1862.

(6) Durharm, D. A.; Frost, G. H.; Hart, F. A. *J. Inorg. Nucl. Chem.* **1969**, *31*, 571.

(7) Arif, A. M.; Hart, F. A.; Hursthouse, M. B.; Thornton-Pett, M.; Zhu, W. *J. Chem. Soc., Dalton Trans.* **1984**, 2449.

(8) Sedney, D.; Kahjehnessiri, M.; Reiff, W. M. *Inorg. Chem.* **1981**, *20*, 3476.

(9) Halfpenny, J.; Small, R. W. H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 939.

(10) (a) Barclay, G. A.; Vagg, R. S.; Watton, E. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 3487. (b) *Ibid.* **1978**, *B34*, 1833. (c) Barclay, G. A.; Vagg, R. S.; Watton, E. C. *Aust. J. Chem.* **1969**, *22*, 643.

(11) (a) Thomas, N. C.; Deacon, G. B. *Inorg. Synth.*, in press. (b) Thomas, N. C.; Deacon, G. B. *Synth. React. Inorg. Met.-Org. Chem.* **1986**, *16*, 85. (c) Deacon, G. B.; Patrick, J. M.; Skelton, B. W.; Thomas, N. C.; White, A. H. *Aust. J. Chem.* **1984**, *37*, 929. (d) Thomas, N. C.; Cox, J. *Polyhedron* **1987**, *7*, 731.

(12) Cleare, M. J.; Griffiths, W. P. *J. Chem. Soc. A* **1969**, *372*.

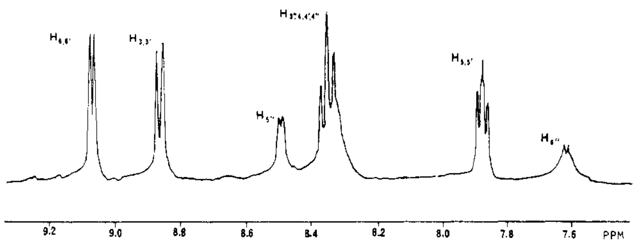


Figure 1. ^{1}H NMR spectrum (400 MHz) and proton assignments for the aromatic region of (μ-TPT)[Ru(CO)$_2$Cl$_2$]$_2$.

putationally stable refinement. There is one independent molecule of II per asymmetric unit and one molecule of methanol per diruthenium complex. Parameters for the collection and refinement of diffraction data are contained in Table I. Unit-cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with $19° \leq 2\theta \leq 25°$.

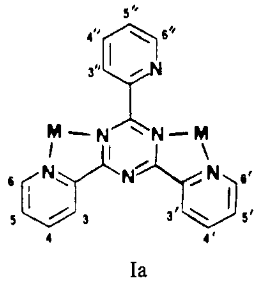
The structure was solved via direct methods (SOLV), which located the ruthenium and chlorine atoms. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated and fixed in idealized positions (d(C–H) = 0.96 Å, $U = 1.2\ U_{iso}$ for the carbon atom to which it was attached). Data were corrected for absorption effects with the program XABS (H. Hope), which corrects data on the basis of deviations between F_o vs F_c values, and trends based upon sin θ, Miller index, or parity group failed to reveal any systematic errors in the data. All computer programs used in the data collection and refinement are contained in the Nicolet XRD (Madison, WI) program packages P3 and SHELXTL (version 5.1). Atomic coordinates are provided in Table II, and selected bond distances and angles are in Table III.

Results and Discussion

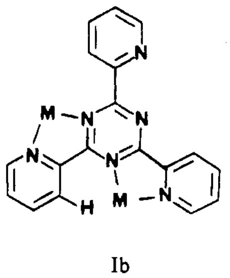
In the absence of light, the reaction of [Ru(CO)$_2$Cl$_2$]$_n$ with TPT in boiling methanol leads to the formation of the diruthenium complex (μ-TPT)[Ru(CO)$_2$Cl$_2$]$_2$ (I, eq 1).

$$2[\mathrm{Ru(CO)_2Cl_2}]_n + \mathrm{TPT} \xrightarrow{\mathrm{MeOH,\ dark}} (\mu\text{-TPT})[\mathrm{Ru(CO)_2Cl_2}]_2 \quad (1)$$

^{1}H NMR, IR, and microanalysis data support the above formulation for I. In addition, the IR band at 1698 cm^{-1} indicates the presence of acetone in the complex, and the NMR peak at δ 2.51, together with analytical data, indicates the complex recrystallizes from acetone containing half a solvent molecule. Of the two possible configurations for the complex (Ia and Ib), structure Ia may be assigned on the basis of the crystal structure of the related complex {μ-C$_3$N$_3$(OMe)(py)$_2$(pyH)}[Ru(CO)$_2$Cl$_2$]$_2$ (below). Formation of Ia rather than the alternative Ib is most likely due to the steric interaction between hydrogen (H$_3$) and the metal in the latter case. No steric hindrance is present in Ia since the uncoordinated pyridine ring is twisted out of the triazine plane. The aromatic region of the ^{1}H NMR spectrum of I is integrated for 12 protons as expected for two magnetically equivalent coordinated pyridyl rings and one inequivalent uncoordinated pyridyl ring. However, only six separate peaks are observed (see Figure 1), due to overlap of resonances, and these may be assigned by comparison with the spectrum of the free TPT. On the basis of the crystal structure of the related complex II (below) and the similar spectroscopic data for I and II, we have assigned cis CO and trans Cl ligands for I.



Ia



Ib

When the reaction between [Ru(CO)$_2$Cl$_2$]$_n$ and TPT in methanol is performed in the light (i.e. in the presence of ordinary laboratory lighting), substitution of methoxide at the TPT triazine ring occurs to yield {μ-C$_3$N$_3$(OMe)(py)$_2$(pyH)}[Ru(CO)$_2$Cl$_2$]$_2$ (II, eq 2).

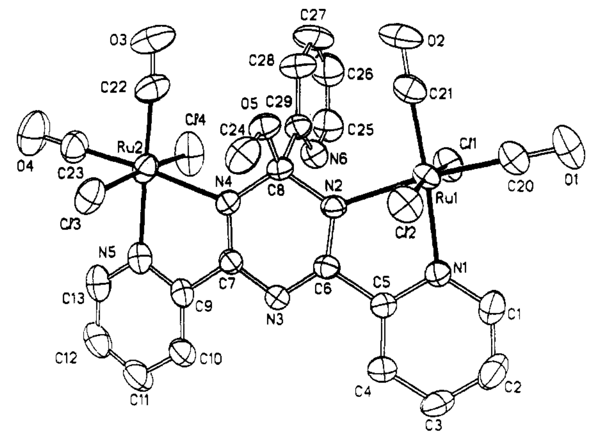


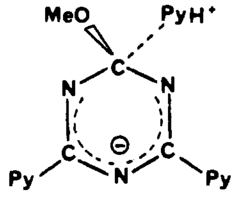
Figure 2. Molecular structure and labeling scheme for {μ-C$_3$N$_3$(MeO)(py)$_2$(pyH)}[Ru(CO)$_2$Cl$_2$]$_2$. Atoms are depicted as 50% probability thermal ellipsoids. A solvation molecule of CH$_3$OH is also included in the crystal lattice.

$$2[\mathrm{Ru(CO)_2Cl_2}]_n + \mathrm{C_3N_3(py)_3} + \mathrm{MeOH} \xrightarrow{h\nu} \{\mu\text{-}\mathrm{C_3N_3(OMe)(py)_2(pyH)}\}[\mathrm{Ru(CO)_2Cl_2}]_2 \quad (2)$$

$$\mathrm{C_3N_3(py)_3} = \mathrm{TPT}$$

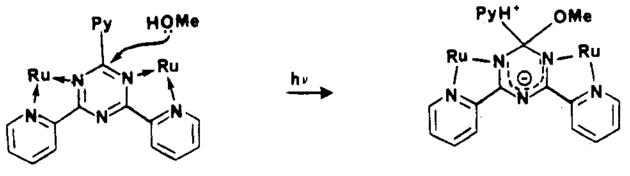
The structure of II has been determined by X-ray crystallography and is shown in Figure 2. The heterocyclic ligand functions as a bis-bidentate ligand to two ruthenium atoms each coordinated to a nitrogen atom of the C$_3$N$_3$ moiety and a pyridinyl nitrogen atom. Complex II contains a pseudo mirror plane that is perpendicular to the central C$_3$N$_3$ ring and contains the groups attached at C(8). The coordination sphere about ruthenium is octahedral with two cis carbonyl groups in the chelation plane and two trans (axial) chlorine atoms.

Methoxide substitution of the triazine ring occurs at C(8). The C$_3$N$_3$ ring C–N distances at C(8) are typical single-bond values (average 1.465 (6) Å), with the remaining four C–N distances narrowly spread in the double-bond range (average 1.329 (6) Å). This latter value is similar to the mean C–N bond distances reported for other TPT complexes, e.g. average 1.36 Å for Hg$_2$(CF$_3$CO$_2$)$_4$(TPT)[9] and average 1.35 Å for [Ni(H$_2$O)$_3$(TPT·HBr)]$^{2+}$.[10a] In addition, the central C$_3$N$_3$ ring is nearly planar, supporting pentadienide delocalized bonding for the five atoms N(2), C(6), N(3), C(7), and N(4):



The pyridyl rings coordinated to Ru(1) and Ru(2) are tilted 10.7 and 10.6°, respectively, from the C$_3$N$_3$ plane in the direction of the pyridyl ring bound at C(8). The central C$_3$N$_3$ ring and this uncoordinated pyridyl ring are near perpendicularly oriented with an interplanar angle of 88.1°. The uncoordinated pyridyl ring is probably protonated, and NMR evidence to support this is given below. However, the crystallographic data were unable to positively identify the presence of the small H$^+$ ion at N(6).

Although TPT usually functions as a tridentate ligand, the bidentate coordination to Ru(CO)$_2$Cl$_2$ is not unexpected. Previously we have reported the reaction of [Ru(CO)$_2$Cl$_2$]$_n$ with terpyridyl yields Ru(CO)$_2$Cl$_2$(tpy), in which the tpy is also coordinated through only two pyridyl rings,[11c] and neither the CO nor the Cl ligands are readily displaced by the free ring to give the chelate complex. In addition, the related complexes Ru(C-



II

Figure 3. Photochemical reaction of MeOH with TPT and $[\mathrm{Ru(CO)_2Cl_2}]_n$. The carbonyl and chloride ligands are omitted for clarity.

$\mathrm{O)_2Cl_2L}$ (L = 1,10-phenanthroline or 2,2′-bipyridyl) are inert to thermal substitution of CO or X by other ligands.[13] Thus, the formation of a bis-bidentate TPT in I and II is consistent with the unreactive nature of the $\mathrm{Ru(CO)_2Cl_2}$ moiety in these compounds.

Spectroscopic data for II are given in the Experimental Section. The IR spectrum contains two strong ν(CO) absorptions in the 1900–2100-cm^{-1} region, indicating cis CO groups. An additional band at 1259 cm^{-1} (which is absent in the spectrum of I) may be assigned to the methoxy C–O–C. The ^{1}H NMR spectrum of II is very similar to that of I but contains an additional broad peak at δ 8.51, which may be attributed to the H$^+$ on the uncoordinated pyridyl ring. The recently developed technique of fast atom bombardment (FAB) mass spectrometry has been used to examine nonvolatile complexes,[14] including some ruthenium compounds,[15] and has been used to determine the mass spectrum of II. The mass spectrum shows the $(M - 1)^+$ peak at m/e 801, due possibly to loss of H from the protonated pyridyl ring, and an ion fragment at m/e 770 due to loss of the methoxy group. In addition, ion fragments corresponding to successive loss of CO and Cl are observed at m/e 735 ($(M - MeO - Cl)^+$), 707 ($(M - MeO - Cl - CO)^+$), 672 ($(M - MeO - 2Cl - CO)^+$), and 644 ($(M - MeO - 2Cl - 2CO)^+$). In general, the observed and calculated isotope distributions are in good agreement for most ion fragments.

The electronic spectra of both I and II in the visible region are very similar, with λ_{max} at ca. 420 nm and due most likely to a $d\pi \rightarrow \pi^*$ (TPT) transition. In methanol, yellow solutions of I and II turn green when exposed to light for 15 min. This color change is accompanied by identical changes in the visible spectra of both I and II, i.e. disappearance of the 420-nm band and appearance of two new bands at 382 (ϵ 4.4 × 10^3) and 583 (ϵ 2.8 × 10^3) nm. Irradiation also produces very complex and near-identical NMR patterns for both compounds in DMSO. However, the solution IR spectra (in $\mathrm{CH_2Cl_2}$) of both complexes before and after irradiation remain essentially unchanged in the ν(CO) stretching region (two strong bands at 2066 and 2004 cm^{-1}). Although we have not yet investigated this photochemical reaction in detail, it appears to be reversible since green solutions of I or II, when left in the dark for several hours, revert back to yellow and possess visible and NMR spectral properties almost identical with those of the original solutions prior to irradiation. The fact that the solution IR spectra are unchanged suggests that the reaction does not involve photoisomerization or photolabilization of the cis CO ligands.

Attempts to isolate II by visible irradiation of I in methanol have been unsuccessful, complex I being recovered unchanged. This would suggest that coordination of TPT to ruthenium and methanol addition possibly occur simultaneously, rather than the former preceding the latter. Although free trisubstituted triazines are stable toward nucleophilic hydrolysis,[16] it has been demonstrated that coordination of trisubstituted triazines, such as TPT, assists nucleophilic attack and hydrolysis of the triazine ring.[17] Coordination of two ruthenium ions to TPT would therefore lead to further destabilization of the triazine ring by enhancing its electron deficiency. (In contrast to the case for benzene, triazines are already electron-deficient, as illustrated by their ease of hydrolysis under relatively mild conditions.[18]) This would encourage the addition of methanol, yielding II (Figure 3). Furthermore, the addition of methanol provides some relief to steric hindrance by making the $\mathrm{C_3N_3}$ C(8) tetrahedral.

The only similar substitution reaction involving coordinated TPT reported is the nucleophilic attack at the triazine ring of $[\mathrm{M(TPT)_2}]^{2+}$ (M = Ni, Co, Fe, Ru) complexes by hydroxide ions in aqueous solution.[19] However, the substituted complexes were only identified in solution by spectroscopic methods. Furthermore, the photosubstitution by methanol has previously been reported for alkenes and several aromatic and heterocyclic molecules (e.g. ref 20). In view of the current interest in photochemical reactions of ruthenium complexes containing N-heterocyclic ligands, our results would suggest further study of ruthenium–TPT complexes is warranted.

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Supplementary Material Available: A full table of crystal data and collection parameters and tables of bond distances and angles, anisotropic temperature factors, hydrogen atom coordinates, and least-squares plane calculations (6 pages); a listing of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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(13) Kingston, J. V.; Jamieson, J. W. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1967**, *29*, 133.

(14) Bojesen, G. *Org. Mass Spectrom.* **1983**, *20*, 413. Miller, J. M. *Adv. Inorg. Chem. Radiochem.* **1984**, *28*, 2.

(15) Miller, J. M.; Balasanmugam, K.; Nye, J.; Deacon, G. B.; Thomas, N. C. *Inorg. Chem.* **1987**, *26*, 560. Thomas, N. C. *Inorg. Chim. Acta* **1987**, *131*, 151.

(16) Smolin, E. M.; Papport, L. *s-Triazines and Derivatives*; Interscience: New York, **1959**; p 44.

(17) Lerner, E. I.; Lippard, S. J. *Inorg. Chem.* **1977**, *16*, 1546.

(18) Grundman, C.; Kreuterger, A. *J. Am. Chem. Soc.* **1954**, *76*, 5646.

(19) Williams, P. A. *Transition Met. Chem.* **1979**, *4*, 24. Gillard, R. D.; Williams, P. A. *Transition Met. Chem.* **1979**, *4*, 18. Gil, V. M. S.; Gillard, R. D.; Williams, P. A.; Vagg, R. S.; Watton, E. C. *Transition Met. Chem.* **1979**, *4*, 14.

(20) Morrison, H.; Nylund, T. *J. Chem. Soc., Chem. Commun.* **1976**, 785. Nzawa, Y.; Tomioka, H.; Kajami, T.; Sato, T. *J. Chem. Soc., Chem. Commun.* **1977**, 780. Kropp, P. J.; Reardon, E. J.; Gaibel, Z. L. F.; Willard, K. F.; Hattaway, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 7058. Shimazaki, M.; Nakamura, H.; Iitaka, Y.; Ohno, M. *Chem. Pharm. Bull.* **1983**, *31*, 3104.

Contribution from the Nuclear Research Centre Negev,
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Equilibrium Constants for the Homolysis of the Metal–Carbon σ Bond in $[(\mathrm{nta})(\mathrm{H_2O})\mathrm{M^{III}CH_3}]^-$ (M = Mn, Fe, Co; nta = Nitrilotriacetate) in Aqueous Solutions

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The effect of the nature of the central cation on the stability of metal–carbon σ bonds in a series of analogous complexes is unknown. In a recent pulse radiolysis study[1] we have measured the equilibrium constant, K

$$[(\mathrm{nta})(\mathrm{H_2O})\mathrm{M^{III}CH_3}]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(\mathrm{nta})(\mathrm{H_2O})_2\mathrm{M^{II}}]^- + {}^{\bullet}\mathrm{CH_3} \qquad (1)$$

$k_{-1}^{\mathrm{Co}} = 1.6 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$ and $K_1^{\mathrm{Co}} = 1.4 \times 10^{-8}$ M for M = Co in aqueous solutions (where nta = nitrilotriacetate). It was shown[1] that $[(\mathrm{nta})(\mathrm{H_2O})\mathrm{M^{III}CH_3}]^-$, for M = Co, decomposes via homolysis followed by

$$[(\mathrm{nta})(\mathrm{H_2O})\mathrm{M^{III}CH_3}]^- + {}^{\bullet}\mathrm{CH_3} \rightarrow [(\mathrm{nta})(\mathrm{H_2O})\mathrm{M^{II}}]^- + \mathrm{C_2H_6} \qquad (2)$$

The results indicated also that the technique enables the study of the effect of substituents on the methyl on K_1 and k_2.[1] It was

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