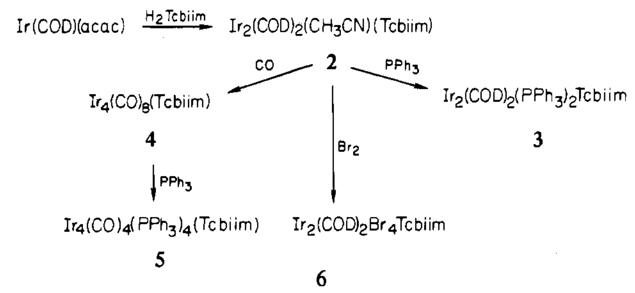
Inorg. Chem. **1984**, *23*, 343–349

Scheme I



samples of the tetracyanobiimidazole tetramers are in the range of insulators.

The rhodium and iridium tetramers with tetracyanobiimidazole react rapidly with bromine in methylene chloride to yield highly insoluble solids. The rhodium complex appears coppery in color while that of the iridium analogue is yellow. Infrared spectra for these two species are essentially identical. These solids are poorly characterized; however, elemental analyses indicate addition of approximately 3 mol of Br_2/tetrameric unit. The tetracyanobiimidazolato-bridged tetramers presumably contain a short intramolecular metal–metal contact similar to that of 2.975 (1) Å observed in $Rh_4(CO)_8(biim)_2$.[4] Perhaps these tetranuclear species can be oxidized to yield complexes with octahedrally coordinated terminal rhodium(III) or iridium(III) ions and stabilized divalent bridging metal ions linked by a metal–metal bond. These oxidized tetramers behave as insulators as determined by the pressed-pellet technique.

Summary

The key intermediate in this series of compounds is clearly the dimer $Ir_2(COD)_2(CH_3CN)(Tcbiim)$ (**2**). As shown in Scheme I, all the other iridium compounds are derivable from it through a series of reactions that show considerable variety. The formation of **2** in acetonitrile results from addition and substitution by solvent at one iridium center on the presumed symmetric quadridentate precursor, since the product contains a three-coordinate $Tcbiim^{2-}$. This reaction suggests that **2** might be a useful material for supporting a catalytic cycle. If **2** is treated with triphenylphosphine, a straightforward addition occurs to yield **3**, but if **2** is treated with carbon monoxide, substitution results and COD is displaced, yielding **4**. These contrasting results suggest that CO is too a strong a π acceptor to allow the iridium(I) to expand its coordination number to 5. However, the carbonyl derivative that forms is a tetramer whose structure is evident from its IR spectrum since it is very similar to the analogous biimidazole compound we reported earlier. These tetramers apparently result from the need for the metals to increase their limited electron density by sharing. Treatment of **4** with triphenylphosphine yields **5**, which has equivalent phosphines by ^{31}P NMR, consistent with addition of the bulky triphenylphosphines to the terminal iridium atoms. If **2** is treated with bromine, oxidative addition occurs and the product **6** containing six-coordinate iridium(III) results.

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Registry No. **1**, 83312-42-9; **2**, 88156-95-0; **3**, 88156-96-1; **4**, 83333-44-2; **5**, 88156-97-2; **6**, 88156-98-3; $Rh_4(CO)_8(Tcbiim)_2$, 88156-99-4.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, atomic thermal parameters, calculated hydrogen positions, and least-squares planes (16 pages). Ordering information is given on any current masthead page.

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Complexes of Tetracyanobiimidazole. 2. Monomeric Species

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In this paper we describe monomeric complexes of Rh(I) and Ir(I) with 4,4′,5,5′-tetracyano-2,2′-biimidazole ($H_2Tcbiim$). These compounds always contain the dianion ($Tcbiim^{2-}$) in accord with the greater acidity expected for the cyano-substituted ring system. The structure of $[NEt_4][Ir(COD)(PPh_3)(Tcbiim)]\cdot CH_2Cl_2$ (COD = 1,5-cyclooctadiene) was determined by X-ray crystallography. The composition $IrC_{45}H_{49}N_9PCl_2$ crystallizes in the $P2_12_12_1$ orthorhombic space group with a = 9.927 (4) Å, b = 11.226 (4) Å, c = 40.119 (13) Å, and Z = 4 molecules/cell. A final agreement of R = 0.048 was obtained for 3010 observed reflections. The structure confirms planar bidentate chelation by $Tcbiim^{2-}$ and an irregular trigonal-bipyramidal coordination for the iridium atom. The preparation of the series of salts $M[Ir(CO)_2(Tcbiim)]$, M = Na^+, K^+, NEt_4^+, NMe_4^+, $C(NH_2)_3^+$, revealed color changes indicative of intermolecular interactions that are cation dependent. The X-ray crystal structure of the red tetraethylammonium salt, $IrC_{20}H_{20}N_9O_2$, was solved in the orthorhombic space group *Pnnm* with a = 7.267 (2) Å, b = 20.697 (8) Å, c = 15.360 (7) Å, and Z = 4 molecules/cell, with a final R = 0.034 for 1284 observed reflections. The planar ions $[Ir(CO)_2(Tcbiim)]^-$ pack in pairs about an inversion center with an Ir–Ir distance of 3.19 Å. These weak intermolecular dimers are in turn packed into slipped stacks with an Ir–Ir distance of 4.728 Å.

Introduction

In a recent preliminary communication[1] we reported the synthesis and properties of the novel new compound 4,4′,5,5′-tetracyano-2,2′-biimidazole ($H_2Tcbiim$, **1**). We have also reported on the dimers and tetramers formed by this ligand with rhodium(I) and iridium(I).[2] In this paper we describe the related monomeric ions. Some of these species are planar ions that show intermolecular interactions in the solid state and in concentrated solution, which are cation dependent. Unlike the analogous biimidazole derivatives we have investigated,[3-5] the monomeric derivatives of tetracyanobiimidazole always contain the dianion rather than the monoprotonated or diprotonated moiety. This is clearly a

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(1) Rasmussen, P. G.; Hough, R. L.; Anderson, J. E.; Bailey, O. H.; Bayón, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6155.

(2) Rasmussen, P. G.; Bailey, O. H.; Bayón, J. C. *Inorg. Chem.*, preceding paper in this issue.

(3) Kaiser, S. W.; Saillant, R. B.; Rasmussen, P. G. *J. Am. Chem. Soc.* **1975**, *97*, 425.

(4) Kaiser, S. W.; Saillant, R. B.; Butler, W. M.; Rasmussen, P. G. *Inorg. Chem.* **1976**, *15*, 2681.

(5) Kaiser, S. W.; Saillant, R. B.; Butler, W. M.; Rasmussen, P. G. *Inorg. Chem.* **1976**, *15*, 2688.

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result of the strongly electron-withdrawing cyano substituents acting on the electronic structure of the imidazole ring system.

Experimental Section

Physical Measurements. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer Model 1330 grating spectrophotometer. Absorbances within visible and ultraviolet regions (200–750 nm) were obtained on a Cary 219 spectrophotometer. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI 49951, or Galbraith Laboratories, Inc., Knoxville, TN 37921. Fourier transform NMR were collected on JEOL FX-90Q and Bruker WM-360 spectrometers. All ^1H and ^{13}C resonances are reported relative to Me_4Si; ^{31}P resonances are reported relative to external phosphoric acid (85%). The dc solid-state electrical resistivities of pressed pellet samples were measured with a Keithley Model 503 milliohmmeter or, for samples with resistances greater than 1000 Ω, a Hewlett-Packard digital ohmmeter was used. Unless otherwise noted, all syntheses and solution manipulations of rhodium(I) and iridium(I) complexes were performed with Schlenk-type apparatus under prepurified nitrogen. Most reactions were nearly quantitative with absolute yield being limited by recovery losses.

Reagents. Solvents were purified by standard methods.[6] $[M(COD)Cl]_2$[7] and $H_2Tcbiim$[1] were prepared by methods previously described. Salts of the dianion of tetracyanobiimidazole were prepared by reacting $H_2Tcbiim$ with the appropriate salts of the aqueous or alcoholic hydroxides or carbonates. All other reagents were used as commercially available.

Preparation of $NEt_4[Rh(COD)(Tcbiim)]$. A mixture of 0.0503 g (0.1020 mmol) of $[Rh(COD)Cl]_2$ and 0.1023 g (0.2076 mmol) of $(NEt_4)_2Tcbiim$ in 20 mL of CH_3CN was heated to reflux for 2 h, yielding a clear yellow solution. After the solution cooled to room temperature, the volume of the solution was reduced by half under reduced pressure with the formation of a yellow microcrystalline solid. Anal. Calcd for $C_{26}H_{32}N_9Rh$: C, 54.45; H, 5.62; N, 21.98. Found: C, 54.34; H, 5.66; N, 21.70.

Preparation of $NEt_4[Rh(CO)_2(Tcbiim)]$. Carbon monoxide was passed through a suspension of 75 mg (0.1221 mmol) of $NEt_4[Rh(COD)(Tcbiim)]$ in 15 mL of CH_3CN for 15 min. During this period the starting material reacted, forming a clear yellow solution. The solution was concentrated under a stream of nitrogen with the formation of fine bright orange needles, which were isolated by filtration. Anal. Calcd for $C_{20}H_{20}N_9O_2Rh$: C, 46.08; H, 3.87; N, 24.18. Found: C, 45.93; H, 3.92; N, 24.09. IR spectrum (cm^{-1}, Nujol): 2081, 2027 (ν_{CO}, s).

Preparation of $NEt_4[Ir(COD)(Tcbiim)]$. The fine orange needles of this compound were prepared by the same method as for its rhodium analogue with 0.9509 g (1.930 mmol) of $(NEt_4)_2Tcbiim$ and 0.6483 g (0.9652 mmol) of $[Ir(COD)Cl]_2$ in 40 mL of CH_3CN. Anal. Calcd for $C_{26}H_{32}N_9Ir$: C, 47.12; H, 4.87; N, 19.02. Found: C, 47.15; H, 4.78; N, 19.18.

Preparation of $C(NH_2)_3[Ir(COD)(Tcbiim)]\cdot 1.5CH_3CN$. A mixture of 0.2700 g (0.7663 mmol) of $[C(NH_2)_3]_2Tcbiim$ and 0.2574 g (0.3832 mmol) of $[Ir(COD)Cl]_2$ in 45 mL of CH_3CN was heated to reflux for 3 h. After the solution cooled to room temperature, the side product $C(NH_2)_3Cl$ was isolated by filtration, yielding a clear orange-brown solution. The volume was reduced under vacuum to 15 mL and cooled to 4 °C for 10 h with formation of an orange-red crystalline solid. Recrystallization from CH_3CN yielded the pure solid. Anal. Calcd for $C_{22}H_{22.5}N_{12.5}Ir$: C, 40.39; H, 3.47; N, 26.76. Found: C, 40.30; H, 3.31; N, 26.71.

Preparation of $NMe_4[Ir(COD)(Tcbiim)]$. This compound was prepared by methods similar to those above except that an additional extraction from acetone was used to separate it from the byproduct NMe_4Cl. Anal. Calcd for $C_{22}H_{24}N_9Ir$: C, 43.55; H, 3.99; N, 20.78. Found: C, 41.21; H, 3.95; N, 18.95.

Preparation of $M[Ir(COD)(Tcbiim)]$, $M = Na^+, K^+$. A mixture of $H_2Tcbiim$, M_2CO_3, and $[Ir(COD)Cl]_2$ in a ratio of 2:2:1 was suspended in CH_3CN and heated to reflux for 3 h with formation of a cloudy orange solution. After the solution cooled to room temperature, the solution was filtered and reduced in volume under vacuum until precipitation just began. Cooling in an ice bath for several hours afforded a bright orange solid, which was isolated by filtration. Anal. Calcd for $C_{18}H_{12}N_8IrNa$: C, 38.92; H, 2.18; N, 20.17. Found: C, 38.91; H, 2.25; N, 20.20. $^{13}C\{^1H\}$ NMR spectrum (acetone-d_6): δ 32.2, 65.3. Anal. Calcd for $C_{18}H_{12}N_8IrK$: C, 37.82; H, 2.12; N, 19.60. Found: C, 37.75; H, 2.26; N, 19.64.

Preparation of $M[Ir(CO)_2(Tcbiim)]$, $M = NEt_4^+, NMe_4^+, C(NH_2)_3^+, Na^+, K^+$. Carbon monoxide was passed through a suspension of approximately 50 mg of $M[Ir(COD)(Tcbiim)]$ in 10 mL of CH_3CN for 15 min. The resulting solution was concentrated under a stream of nitrogen and the product isolated by filtration: $M = NEt_4^+$, bright red needles; $M = NMe_4^+$, green; $M = C(NH_2)_3^+, Na^+, K^+$, dark blue-black solids. Anal. Calcd for $C_{20}H_{20}N_9O_2Ir$: C, 39.34; H, 3.30; N, 20.64. Found: C, 39.16; H, 3.23; N, 20.69. IR spectrum (cm^{-1}, Nujol): 2063, 2013 (ν_{CO}, s). Anal. Calcd for $C_{16}H_{12}N_9O_2Ir$: C, 34.66; H, 2.18; N, 22.73. Found: C, 34.63; H, 2.16; N, 22.68. IR spectrum (cm^{-1}): 2082 (vs), 2052 (s), 2032 (s), 2021 (s), 2013 (s), 1989 (s) (ν_{CO} Nujol); 2076, 2007 (ν_{CO}, s, CH_3CN solution). Anal. Calcd for $C_{13}H_6N_{11}O_2Ir$: C, 28.89; H, 1.12; N, 28.51. Found: C, 28.57; H, 1.13; N, 28.31. IR spectrum (cm^{-1}, Nujol): 2098, 2033 (ν_{CO}, s). Anal. Calcd for $C_{12}H_4N_8O_4IrNa$ (dihydrate): C, 26.72; H, 0.75; N, 20.77; Na, 4.26. Found: C, 27.29; H, 0.85; N, 20.86; Na, 4.18. IR spectrum (cm^{-1}, Nujol: 2099, 2037 (ν_{CO}, s). $^{13}C\{^1H\}$ NMR spectrum (acetone-d_6, 0.1 M $Cr(acac)_3$): δ 172.2, 153.6, 123.7, 119.8, 113.8, 112.5. Anal. Calcd for $C_{12}N_8O_2IrK$: C, 27.75; H, 0.00; N, 21.57. Found: C, 27.76; H, 0.08; N, 21.46. IR spectrum (cm^{-1}, Nujol): 2097, 2040 (ν_{CO}, s).

Preparation of $NEt_4[Ir(CO)_2Br_2(Tcbiim)]$. Several drops of bromine were added to a suspension of 0.1000 g (0.1519 mmol) of $NEt_4[Ir(CO)_2(Tcbiim)]$ in CH_2Cl_2. After several minutes of stirring, the solution was reduced to dryness under vacuum to remove any excess Br_2. The remaining solid was redissolved in $CHCl_3$ and the process repeated several times. Finally, the solid was rinsed with petroleum ether repeatedly and dried under vacuum. Anal. Calcd for $C_{26}H_{32}N_9Br_2Ir$: C, 31.18; H, 2.62; N, 16.36; Br, 20.74. Found: C, 31.26; H, 2.82; N, 16.21; Br, 20.70. IR spectrum (cm^{-1}, Nujol): 2156, 2132, 2115, 2085 (ν_{CO}, s).

Preparation of $NEt_4[Ir(COD)(PPh_3)(Tcbiim)]\cdot CH_2Cl_2$. A mixture of 0.0978 g (0.1506 mmol) of $NEt_4[Ir(COD)(Tcbiim)]$ and 0.0395 g (0.1506 mmol) of PPh_3 was stirred in 10 mL of CH_3CN for 15 min with the formation of a pale yellow solution. The solvent was removed under vacuum and the resulting pale yellow solid redissolved in 7 mL of CH_2Cl_2. This solution was filtered and several mL of hexane added until the solution became slightly cloudy. When the solution was cooled overnight at 4 °C, crystals formed, which were isolated by filtration. Anal. Calcd for $C_{45}H_{49}N_9Cl_2PIr$: C, 53.51; H, 4.89; N, 12.48; P, 3.07. Found: C, 53.34; H, 4.80; N, 12.36; P, 2.98. NMR spectra ($CDCl_3$): ^{31}P, δ 12.4; $^{13}C\{^1H\}$, δ 7.7, 53.0, 60.8, 32.3, 129.4 (b), 128 d, $|J_{PC}| = 9.1$ Hz, 133.7 d, $|J_{PC}| = 12.0$ Hz, 128.3, 153.1, 114.1 (w), 118.5 (w).

Crystal Structure Determinations. $NEt_4[Ir(COD)(PPh_3)(Tcbiim)]\cdot CH_2Cl_2$. Data Collection and Reduction. Single crystals of $NEt_4[Ir(COD)(PPh_3)(Tcbiim)]\cdot CH_2Cl_2$ were grown by adding 5 mL of hexane to 10 mL of a concentrated solution of the compound in methylene chloride and cooling to 4 °C in a refrigerator. Within 48 h, several large yellow prisms had formed. A portion of one of these crystals was shaped nearly spherically and sealed in a 0.3-mm diameter glass capillary and mounted on a $P\bar{1}$ diffractometer. The space group $P2_12_12_1$ was confirmed by the successful solution of the structure. A summary of the crystal data as well as parameters for data collection can be found in Table I. Following standardization of reflection intensities fo compensate for crystal decomposition, data were reduced by methods described previously.[8]

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(7) (a) Shriver, D. F., Ed. *Inorg. Synth.* **1979**, *19*, 218. (b) Winkhaus, G.; Singer, H. *Chem. Ber.* **1966**, *99*, 3610.

(8) Computer programs used during the structural analysis were SYNCOR (data reduction by W. Shmonsees), N. W. Alcock's absorption program, FORDAP (Fourier synthesis by A. Zalkin), ORFLS (full-matrix least-squares refinement by Busing, Martin, and Levy), ORFFE (distances, angles, and their esd's by Busing, Martin, and Levy), ORTEP (thermal ellipsoid drawings by C. K. Johnson), HATOMS (hydrogen atom positions by A. Zalkin), PLANES (least squares by D. M. Blow), and PLUTO (crystallographic plotting program supplied by University Chemical Laboratory, Cambridge, England). Atomic scattering factors were obtained from: Cromer, D. T.; Weber, J. T. *Acta Crystallogr.* **1965**, *18*, 104. Anomalous dispersion correction terms f' and f'' for iridium were taken from: MacGillavry, C. H.; Reich, C. D.; Lonsdale, K., "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1962, Vol. III, p 201.

Table I. Crystallographic Parameters for NEt$_4$[Ir(COD)(PPh$_3$)(Tcbiim)]·CH$_2$Cl$_2$

space group	$P2_12_12_1$
a, Å	9.927 (4)
b, Å	11.226 (4)
c, Å	40.119 (13)
V, Å^3	4470.6 (30)
mw	1010.05
Z	4
d_{obsd}, g/cm^3	1.52 (1)
d_{calcd}, g/cm^3	1.500
cryst dimens, mm	0.23-0.29
cryst shape	prismatic but shaped nearly spherically
radiation, Å	λ(Mo Kα) 0.710 69, graphite monochromator
linear abs coeff, (Mo Kα), cm^{-1}	31.719
transmission factors	0.40-0.48
scan speed, deg/min	variable, 2.5-12, determined as a function of peak intens
% dev of stds during data collection	11
2θ limit, deg	50
reflcns collected	4804
reflcns with $F^2 \geqslant 3\sigma(F^2)$	3010

Table II. Crystallographic Parameters for NEt$_4$[Ir(CO)$_2$(Tcbiim)]

space group	$Pnnm$
a, Å	7.267 (2)
b, Å	20.697 (8)
c, Å	15.360 (7)
V, Å^3	2310.2 (20)
mw	610.66
Z	4
d_{obsd}, g/cm^3	1.76 (1)
d_{calcd}, g/cm^3	1.756
cryst dimens, mm	(001), 0.232; (010), 0.090; (001), 0.225
cryst shape	plates
radiation, Å	λ(Mo Kα) 0.710 69, graphite monochromator
linear abs coeff, μ(Mo Kα), cm^{-1}	57.924
transmission factors	0.27-0.52
scan speed, deg/min	variable, 2.5-12, function of peak height
% dev of stds during data collection	2
2θ limit, deg	45
reflcns collected	1912
reflcns with $F^2 \geqslant 3\sigma(F^2)$	1284

Table III. Fractional Atomic Coordinates for NEt$_4$[Ir(COD)(PPh$_3$)(Tcbiim)]·CH$_2$Cl$_2$

atom	x	y	z
Ir	0.2114 (1)	0.1003 (1)	0.1236 (0)
P	0.0912 (5)	0.0227 (4)	0.0780 (1)
C11	−0.0067 (17)	0.1417 (14)	0.0564 (4)
C12	−0.1102 (20)	0.1943 (17)	0.0748 (6)
C13	−0.1772 (20)	0.2924 (20)	0.0609 (6)
C14	−0.1432 (23)	0.3313 (21)	0.0294 (6)
C15	−0.0347 (27)	0.2819 (22)	0.0128 (6)
C16	0.0298 (21)	0.1866 (17)	0.0263 (5)
C21	0.1951 (19)	−0.0474 (14)	0.0449 (4)
C22	0.1294 (20)	−0.0894 (18)	0.0171 (5)
C23	0.2027 (28)	−0.1508 (17)	−0.0080 (5)
C24	0.3364 (26)	−0.1642 (17)	−0.0047 (6)
C25	0.4007 (22)	−0.1226 (21)	0.0239 (6)
C26	0.3269 (18)	−0.0610 (16)	0.0477 (5)
C31	−0.0247 (17)	−0.0967 (18)	0.0860 (4)
C32	0.0321 (21)	−0.2120 (18)	0.0948 (5)
C33	−0.0561 (25)	−0.3046 (20)	0.1018 (5)
C34	−0.1908 (26)	−0.2924 (21)	0.1019 (5)
C35	−0.2437 (17)	−0.1908 (23)	0.0941 (6)
C36	−0.1647 (18)	−0.0930 (20)	0.0864 (5)
N1	0.0169 (14)	0.1312 (10)	0.1545 (4)
C2	−0.0033 (15)	0.0397 (14)	0.1759 (4)
N3	−0.1060 (14)	0.0484 (12)	0.1972 (4)
C4	−0.1567 (18)	0.1601 (18)	0.1883 (5)
C5	−0.0837 (17)	0.2077 (16)	0.1635 (5)
C6	−0.2712 (20)	0.2081 (16)	0.2049 (5)
C7	−0.1020 (24)	0.3224 (20)	0.1483 (6)
N4	−0.3640 (20)	0.2490 (16)	0.2176 (5)
N5	−0.1252 (25)	0.4111 (15)	0.1368 (5)
N1′	0.1862 (12)	−0.0586 (12)	0.1513 (3)
C2′	0.0840 (17)	−0.0620 (13)	0.1745 (4)
N3′	0.0858 (14)	−0.1582 (13)	0.1934 (4)
C4′	0.1862 (17)	−0.2211 (14)	0.1822 (4)
C5′	0.2511 (14)	−0.1627 (15)	0.1553 (4)
C6′	0.2259 (24)	−0.3358 (18)	0.1939 (5)
C7′	0.3620 (20)	−0.2068 (18)	0.1349 (5)
N4′	0.2522 (24)	−0.4258 (15)	0.2053 (5)
N5′	0.4434 (16)	−0.2405 (16)	0.1195 (5)
C41	0.2921 (22)	0.2236 (15)	0.0874 (4)
C42	0.2093 (24)	0.2821 (14)	0.1100 (4)
C43	0.2630 (21)	0.3582 (13)	0.1378 (5)
C44	0.3681 (22)	0.2969 (17)	0.1596 (5)
C45	0.3535 (18)	0.1604 (16)	0.1593 (4)
C46	0.4178 (15)	0.0873 (18)	0.1365 (4)
C47	0.5133 (19)	0.1412 (20)	0.1085 (5)
C48	0.4510 (21)	0.2353 (21)	0.0884 (6)
N6	0.2728 (17)	0.1806 (12)	0.2816 (4)
C51	0.3925 (19)	0.0982 (22)	0.2842 (5)
C52	0.1431 (20)	0.1253 (17)	0.2956 (5)
C53	0.2961 (26)	0.2961 (17)	0.3013 (5)
C54	0.2553 (21)	0.2066 (19)	0.2455 (5)
C55	0.4194 (21)	0.0564 (19)	0.3211 (6)
C56	0.0977 (24)	0.0085 (18)	0.2780 (6)
C57	0.4165 (27)	0.3648 (19)	0.2886 (7)
C58	0.1392 (22)	0.2853 (25)	0.2371 (5)
C8	0.1918 (33)	0.5205 (25)	0.0391 (7)
Cl1	0.2424 (10)	0.4944 (10)	0.0008 (4)
Cl2	0.3277 (17)	0.5672 (9)	0.0616 (3)

Solution and Refinement. This structure was solved by conventional Patterson and Fourier syntheses. The correct sign of the anomalous scattering factors was determined, and two cycles of least-squares refinement of the scale factor and individual positional and isotropic thermal parameters led to convergence with $R = 0.066$ and $R_w = 0.075$. Continued refinement using anisotropic thermal parameters for all non-hydrogen atoms led to convergence with $R = 0.052$ and $R_w = 0.061$. Idealized hydrogen atom coordinates and temperature factors, as well as their contributions to the structure factors, were calculated and led to final values of R and R_w equal to 0.048 and 0.051, respectively. In the final difference Fourier map no peak greater than 1.35 e Å^{-3} was observed.

NEt$_4$[Ir(CO)$_2$(Tcbiim)]. Data Collection and Reduction. Light red crystals of NEt$_4$[Ir(CO)$_2$(Tcbiim)] were grown by evaporation of a solution of the complex in CH$_3$CN. Systematic absences corresponded to the space group $Pnnm$. Selected parameters used in data collection are summarized in Table II. Data were reduced by methods previously described.[8]

Solution and Refinement. This structure was solved by direct methods. Following location of the iridium position, two cycles of Fourier difference map synthesis and refinement of new atomic positions yielded the coordinates of all non-hydrogen atoms. After refinement to isotropic convergence ($R = 0.085$, $R_w = 0.103$), the data were corrected for absorption and the terms for anomalous scattering introduced ($R = 0.048$, $R_w = 0.059$). Continued refinement using anisotropic thermal parameters led to convergence with $R = 0.039$, $R_w = 0.048$. Hydrogen atom coordinates and temperature factors were calculated as described above, and the structure was refined to final convergence with R and R_w equal to 0.034 and 0.041, respectively. The final difference map showed no peak greater than 1.62 e Å^{-3}—the largest peaks being residuals of the iridium atom.

Descriptions of the Structures

NEt$_4$[Ir(COD)(PPh$_3$)(Tcbiim)]·CH$_2$Cl$_2$. The molecular structure of the complex anion [Ir(COD)(PPh$_3$)(Tcbiim)]$^-$ is shown in Figure 1. Only the α-carbons of the phenyl rings are displayed in order to allow an unhindered view of the

Table IV. Fractional Atomic Coordinates for $NEt_4[Ir(CO)_2(Tcbiim)]$

atom	*x*	*y*	*z*
Ir1	0.307 87 (6)	0.463 12 (2)	0.0 (0)
N1	0.216 98 (86)	0.534 74 (33)	0.085 01 (41)
C2	0.1484 (10)	0.588 99 (43)	0.047 50 (51)
N3	0.090 49 (96)	0.634 45 (32)	0.101 37 (42)
C4	0.1215 (11)	0.607 43 (45)	0.180 64 (48)
C5	0.1979 (11)	0.546 50 (42)	0.172 05 (55)
C6	0.0747 (13)	0.640 75 (43)	0.258 78 (57)
C7	0.2450 (13)	0.501 54 (50)	0.240 62 (61)
N4	0.0394 (12)	0.667 08 (43)	0.321 44 (55)
N5	0.2819 (14)	0.471 05 (43)	0.297 75 (64)
C8	0.3678 (13)	0.401 85 (58)	0.083 49 (61)
O8	0.3982 (12)	0.363 12 (35)	0.133 64 (46)
N6	0.4602 (15)	0.328 51 (47)	0.500 00 (0)
C11	0.5385 (13)	0.294 15 (41)	0.421 73 (55)
C12	0.2511 (18)	0.327 37 (77)	0.500 00 (0)
C13	0.5138 (22)	0.401 97 (65)	0.500 00 (0)
C21	0.4727 (14)	0.318 79 (53)	0.334 83 (59)
C22	0.1618 (20)	0.263 44 (80)	0.500 00 (0)
C23	0.7162 (25)	0.414 98 (72)	0.500 00 (0)

Table V. Interatomic Distances (Å, with Esd's) for $NEt_4[Ir(COD)(PPh_3)(Tcbiim)]\cdot CH_2Cl_2$

Metal-Ligand and P-C Distances			
Ir-P	2.352 (5)	Ir-C45	2.122 (17)
Ir-N1	2.322 (15)	Ir-C46	2.118 (15)
Ir-N1′	2.116 (13)	Ir-B[a]	2.005 (15)
Ir-C41	2.160 (16)	P-C11	1.866 (17)
Ir-C42	2.113 (15)	P-C21	1.856 (18)
Ir-A[a]	2.021 (15)	P-C31	1.795 (20)
Carbon-Carbon Distances within the C_8H_{12} Ligand			
C41-C42	1.389 (26)	C45-C46	1.386 (23)
C42-C43	1.502 (24)	C46-C47	1.589 (24)
C43-C44	1.526 (27)	C47-C48	1.466 (28)
C44-C45	1.539 (26)	C48-C41	1.583 (27)
Distances within the $Tcbiim^{2-}$ Ligand			
N1-C2	1.355 (18)	N1′-C2′	1.378 (20)
C2-N3	1.333 (20)	C2′-N3′	1.319 (19)
N3-C4	1.397 (22)	N3′-C4′	1.301 (21)
C4-C5	1.343 (26)	C4′-C5′	1.418 (21)
C5-N1	1.365 (21)	C5′-N1′	1.345 (18)
C4-C6	1.422 (25)	C4′-C6′	1.426 (27)
C5-C7	1.438 (29)	C5′-C7′	1.459 (24)
C6-N4	1.149 (23)	C6′-N4′	1.141 (23)
C7-N5	1.121 (26)	C7′-N5′	1.085 (22)
N1-N1′	2.717 (18)	N3-N3′	3.005 (19)
C2-C2′	1.435 (21)		

[a] A is the midpoint of C41-C42 and B is the midpoint of C45-C46.

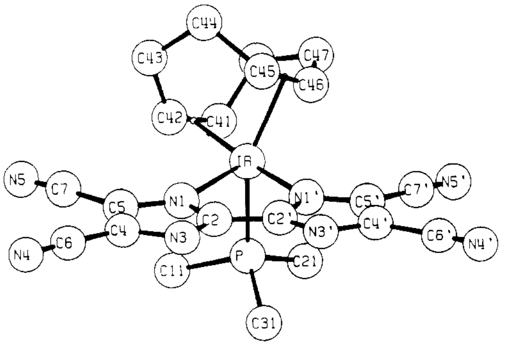

Figure 1. Structure of $NEt_4[Ir(COD)(PPh_3)(Tcbiim)]\cdot CH_2Cl_2$.

metal's coordination geometry. Pertinent intramolecular bond distances and angles are presented in Tables V and VI.

Table VI. Interatomic Angles (deg) for $NEt_4[Ir(COD)(PPh_3)(Tcbiim)]\cdot CH_2Cl_2$

Angles about the Iridium Atom			
P-Ir-N1	92.9 (3)	N1-Ir-A	107.3
P-Ir-N1′	92.1 (4)	N1′-Ir-A	175.4
A-Ir-B	87.8	N1-Ir-B	116.1
P-Ir-A	91.6	N1′-Ir-B	87.6
P-Ir-B	150.0	N1-Ir-N1′	75.3 (5)
Angles within the $Tcbiim^{2-}$ Ligand			
C2-N1-C5	101.6 (15)	C2′-N1′-C5′	104.3 (13)
N3-C2-N1	117.6 (14)	N3′-C2′-N1′	113.7 (14)
N3-C2-C2′	123.1 (14)	N3′-C2′-C2	129.5 (15)
N1-C2-C2′	119.3 (14)	N1′-C2′-C2	116.7 (14)
C4-N3-C2	100.3 (15)	C4′-N3′-C2′	104.9 (14)
N3-C4-C5	110.6 (18)	N3′-C4′-C5′	111.1 (14)
N3-C4-C6	120.7 (20)	N3′-C4′-C6′	126.0 (16)
C6-C4-C5	128.8 (20)	C6′-C4′-C5′	122.8 (18)
C4-C5-N1	109.9 (17)	C4′-C5′-N1′	106.0 (14)
C4-C5-C7	127.2 (18)	C4′-C5′-C7′	127.9 (17)
N1-C5-C7	122.9 (17)	N1′-C5′-C7′	126.1 (16)
C4-C6-N4	178.4 (22)	C4′-C6′-N4′	174.8 (25)
C5-C7-N5	175.3 (28)	C5′-C7′-N5′	179.2 (27)
Angles within the C_8H_{12} Ligand			
C48-C41-C42	122.3 (18)	C44-C45-C46	123.4 (18)
C41-C42-C43	122.9 (20)	C45-C46-C47	121.1 (18)
C42-C43-C44	114.3 (15)	C46-C47-C48	114.3 (16)
C43-C44--C45	112.4 (16)	C47-C48-C41	112.0 (17)

Table VII. Interatomic Distances (Å, with Esd's) for $NEt_4[Ir(CO)_2(Tcbiim)]$

Ir1-C8	1.855 (12)	C8-O8	1.134 (11)
Ir1-N1	2.083 (6)	N6-C11	1.508 (10)
N1-C2	1.357 (10)	N6-C12	1.520 (16)
N1-C5	1.366 (11)	N6-C13	1.570 (17)
C2-N3	1.322 (10)	C11-C21	1.507 (12)
C2-C2′	1.456 (16)	C12-C22	1.473 (21)
N3-C4	1.359 (10)	C13-C23	1.496 (21)
C4-C5	1.384 (12)	N1-N1′	2.611 (13)
C4-C6	1.425 (12)	N3-N3′	3.114 (13)
C5-C7	1.446 (14)	Ir1-Ir1	3.182 (1)
C6-N4	1.135 (10)	Ir1-Ir1	4.728 (2)
C7-N5	1.114 (12)		

The pentacoordinate geometry about the central iridium atom is best described as a distorted trigonal bipyramid with the three equatorial positions taken up by the P of the triphenylphosphine ligand, the midpoint B of an olefin (C45–C46) group, and a nitrogen atom (N1) of the bidentate tetracyanobiimidazole dianion. The axial sites are occupied by the remaining olefinic (C41–C42) midpoint A and nitrogen atom (N1′) of the tetracyanobiimidazole ligand.

The greatest distortion of the trigonal bipyramid stems from the bulkiness of the triphenylphosphine ligand within the equatorial plane. Angles between the ligands of the equatorial plane range from 93 to 150°—the sum being 359°. The largest of these angles allows room for the fan of phenyl rings to avoid the "tub" of the cyclooctadiene ligand and the nitriles of $Tcbiim^{2-}$. Angles between the axial and equatorial ligands vary from 75.3 to 107.3°. Here the greatest deviation from the idealized geometry results from the reduced angle of the bite of the tetracyanobiimidazole dianion (75.3°).

The Ir–P distance of 2.352 Å compares well with values found for PPh_3 in other trigonal-bipyramidal complexes of Ir(I) (2.308–2.403 Å),[9] as does the bonding of the olefin groups.

The Ir–N distances are significantly different, the axial bond length (2.113 Å) being shorter than the equatorial bond length (2.322 Å). Similar type behavior has been observed in (fumaronitrile)(8-methoxycyclooct-4-enyl)(1,10-phenanthroline)iridium(I) and in $(COD)_2Ir(SnCl_3)$.[10-12]

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Table VIII. Interatomic Angles (deg) for $NEt_4[Ir(CO)_2(Tcbiim)]$

C8-Ir1-C8	87.45 (60)	N1-C5-C7	125.03 (18)
C8-Ir1-N1	97.33 (37)	C4-C5-C7	127.70 (80)
C8-Ir1-N1	173.80 (32)	N4-C6-C4	179.20 (14)
N1-Ir1-N1	77.64 (37)	N5-C7-C5	174.40 (11)
C2-N1-C5	103.35 (67)	O8-C8-Ir1	177.26 (95)
N3-C2-N1	116.11 (68)	C11-N6-C11	105.69 (92)
N3-C2-C2	128.76 (45)	C11-N6-C12	111.73 (67)
N1-C2-C2	115.13 (43)	C11-N6-C13	111.27 (65)
C2-N3-C4	102.42 (68)	C12-N6-C13	105.30 (10)
N3-C4-C5	110.86 (71)	C21-C11-N6	115.25 (72)
N3-C4-C6	121.05 (80)	C22-C12-N6	117.00 (12)
C5-C4-C6	128.08 (78)	C23-C13-N6	114.70 (12)
N1-C5-C4	107.23 (72)		

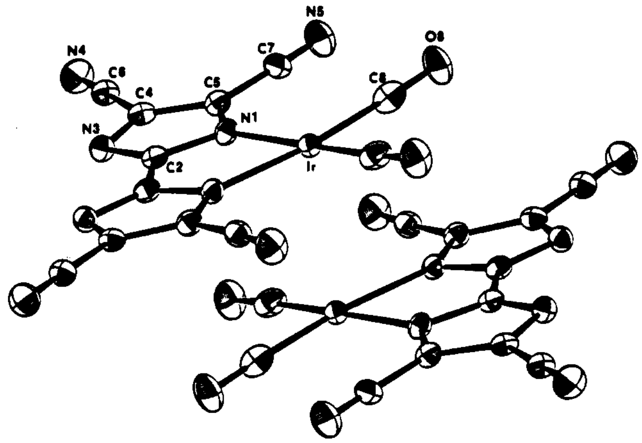

Figure 2. Structure of $NEt_4[Ir(CO)_2(Tcbiim)]$.

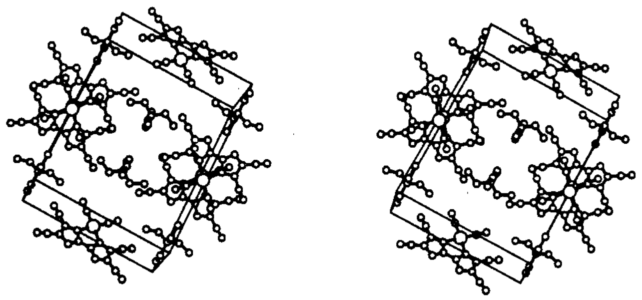

Figure 3. Unit cell of $NEt_4[Ir(CO)_2(Tcbiim)]$.

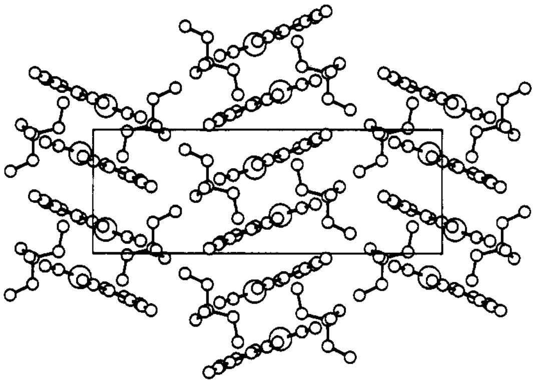

Figure 4. Stacking of $NEt_4[Ir(CO)_2(Tcbiim)]$ viewed along the *b* axis.

As a tetradentate bridge, internal N-M-N angles of 82.5 (2) and 82.78°, as well as N-N bidentate distances of 2.818 and 2.860 Å, have been observed for $biim^{2-}$ with Rh[4] and Cu,[12] respectively.

As a simple bidentate,[13] or as a tetradentate bridge between three metal atoms,[5] rotation of the imidazolato rings reduces the bite angle to 80.7 (4) and 78.7 (2)° and the bidentate distance to 2.744 and 2.625 Å, respectively. The smaller angle in $NEt_4[Ir(COD)(PPh_3)(Tcbiim)]$ also results from its longer metal-nitrogen bond lengths.

$NEt_4[Ir(CO)_2(Tcbiim)]$. The molecular structure of the complex anion is displayed in Figure 2. Tables VII and VIII contain pertinent intramolecular distances and angles.

The anion is strictly planar. A least-squares calculation shows no atom to deviate more than 0.086 Å from the molecule's best plane. The nitrogen of the tetraethylammonium cation is also nearly coplanar with the anion in addition to lying within a mirror plane. Two of the ethyl groups also lie in this same mirror plane. Another ethyl group and its mirror-related counterpart complete the cation.

The geometry about Ir1 is distorted from idealized square planar coordination due to the bite angle (77.6 (4)°) of the bidentate $Tcbiim^{2-}$ ligand. Although the angle between carbonyl ligands is nearly 90°, the N1-Ir1-C8 angle of 97.3 (4)° compensates for the smaller angle produced by the reduced bite of the $Tcbiim^{2-}$.

The Ir-N1 bond length (2.083 (16) Å) is very nearly equal to those observed in the iridium dimer $Ir_2(COD)_2(CH_3CN)(Tcbiim)$ (2.087 (10), 2.094 (10) Å).[2]

The most interesting feature of this structure is the packing of these molecules within the crystal (Figures 3 and 4). An inversion center located near Ir1 generates another complex anion in a parallel plane such that a short intermolecular metal-metal distance of 3.183 (1) Å is obtained. The ligands of this "dimeric" unit are positioned so that the carbonyl carbons are eclipsed by the nitrogens (N1) of the adjacent $Tcbiim^{2-}$ ligand. The carbonyl oxygens lie above (or below) the imidazole rings.

These dimers are arranged in stacks; however, since the plane of the complex anion is not parallel to the *bc* plane, the axis of the stack is not collinear with the Ir-Ir vector of the dimeric unit. As a result of this, the shortest Ir-Ir distance between two different dimers is 4.728 (2) Å.

As mentioned previously, the nitrogen of the tetraethylammonium cation is nearly in the same plane as the complex anion. It is also located in the mirror plane parallel to the *ab* plane. This same mirror plane generates adjacent stacks of complexes along the *c* axis. For this reason all molecules at a given level in the stack (same *a*) have the same spatial orientation. The cation sits in a hole on the carbonyl side of the molecule between these adjacent stacks with the symmetry-related ethyl groups appearing to span from carbonyl to carbonyl.

Adjacent molecules in adjacent stacks zigzag along the *b* axis as shown in Figure 4. This view also allows one to see how the other ethyl groups of the cation extend from the carbonyl ends of a pair of molecules toward a position central to the nitriles of the $Tcbiim^{2-}$ ligands of the inversion-related molecules. Interestingly, this zigzag direction is also the direction of slowest crystal growth and crystal growth is most rapid along the stacking direction.

Results

Upon heating acetonitrile solutions of $[M(COD)Cl]_2$ and tetracyanobiimidazole in the presence of carbonate salts, complexes of the type $M'[M(COD)(Tcbiim)]$ are obtained (M = Rh, M′ = NEt_4^+; M = Ir, M′ = NEt_4^+, NMe_4^+, $CH_6N_3^+$, K^+, and Na^+). Alternatively, salts of the dianion of tetracyanobiimidazole, $M'_2Tcbiim$, may be used in place of $H_2Tcbiim$ and M'_2CO_3. The rhodium salt forms bright yellow prisms while those of the iridium complexes are bright orange.

The infrared spectra of the various salts display absorbances attributed to the chelating COD ligand as determined by

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comparison to the spectra of $[M(COD)Cl]_2$. A splitting (10 cm^{-1}) in the absorption associated with the stretching of the nitriles (2220 cm^{-1}) is often observed in spectra of complexes containing the dianion of tetracyanobiimidazole. The broadness of this stretch in the sodium and potassium salts of this complex is attributed to packing interactions in the solid state as evidenced by the sharp absorbance obtained on samples dissolved in THF.

Although resonances due to the $Tcbiim^{2-}$ carbons were not observed in the proton-decoupled ^{13}C NMR spectrum of Na[Ir(COD)(Tcbiim)], singlets at 65.3 and 32.2 ppm are assigned to the olefinic and aliphatic carbons of the COD ligand, respectively. As expected, the chemical shift of the olefinic COD carbons is affected to a greater extent than that of the aliphatic carbons upon complexation. Singlets at 128.7 and 28.3 ppm are observed for the free ligand[14] whereas, upon complexation with square-planar iridium(I), these carbons resonate at 52.3–70.7 and 28.6–33.1 ppm, depending upon the ligands trans to the olefinic linkages.[15]

Triphenylphosphine reacts with NEt_4[Ir(COD)(Tcbiim)] to yield a highly soluble yellow complex, $NEt_4[Ir(COD)(PPh_3)(Tcbiim)]$. Even when this compound is heated in excess triphenylphosphine, the cyclooctadienyl ligand is not displaced.

The proton-decoupled ^{13}C NMR spectrum obtained in $CDCl_3$ reflects the fluxionality of this pentacoordinate species. In addition to the resonances due to the tetraethylammonium cation, only two singlets attributed to the olefinic and aliphatic carbons of the COD ligand are observed. Resonances of the phenyl carbons along with their phosphorus couplings are also observable. This type of ligand exchange has been studied in other pentacoordinate complexes of iridium and rhodium containing cyclooctadienyl and phosphine ligands.[16] All chemical shifts and coupling constants are in ranges typical of these ligands in similar complexes.[15,17]

Carbon monoxide readily displaces the neutral cyclooctadienyl ligand when bubbled through suspensions of the salts of $[Ir(COD)(Tcbiim)]^-$ in acetonitrile. In the infrared spectra of the resulting monomeric salts, $M'[M(CO)_2(Tcbiim)]$, all peaks lie in the appropriate range for terminal carbonyls bound to rhodium (1953–2904 cm^{-1})[18,19] and iridium (1944–2097 cm^{-1}).[17,19] The frequencies of these stretches are known to depend on the central metal ion;[20] however, in these salts the dependence upon the cation is equally significant.

The tetramethylammonium salt exhibits peculiar behavior in the carbonyl region of its infrared spectrum. Six separate absorbances are observed in a Nujol-supported mull ranging from 2082 to 1989 cm^{-1}. Only two peaks appear in a solution spectrum obtained in acetonitrile, showing that these bands are due to solid-state effects. Similar effects have been observed in systems containing cis dicarbonyls and relatively planar β-diketonate and related Schiff base derivatives.[19-21] These absorbances have been attributed to a lowering of symmetry upon formation of intramolecular metal–metal interactions.[20,22]

In very dilute solution the complex anion is independent of cation. The electronic absorption spectra obtained on dilute solutions of several salts of $[Ir(CO)_2(Tcbiim)]^-$ in acetonitrile are equivalent. As these solutions become more concentrated, they become intensely colored. The more soluble complex salts (those with smaller cations such as K^+ or Na^+) appear almost blue-black. A similar situation has been observed for salts of isocyanide complexes of Rh and Ir, for which absorbances associated with dimeric and trimeric species have been identified.[23]

Solution spectra of $Na[Ir(CO)_2(Tcbiim)]$ show a similar type of behavior. New absorption bands grow in at higher concentrations, which are attributed to an intermolecular charge transfer between associated monomers such as those observed in the solid state for $NEt_4[Ir(CO)_2(Tcbiim)]$. A detailed spectroscopic study is in progress to elucidate the thermodynamic quantities associated with this equilibrium.

The colors of these planar complexes in the solid state are also suggestive of *a* stacks with metal–metal interactions. Studies on the precursors of the partially oxidized tetracyanoplatinates show a direct relationship between the colors of the solids and the intermolecular metal–metal distances within a stack.[10] As the size of the cation is reduced, allowing more compact stacking arrangements, the colors of the resulting solids change from yellow to red. This same type of behavior is observed in the salts of $M'[Ir(CO)_2(Tcbiim)]$: NEt_4^+, bright red; NMe_4^+, green; $C(NH_2)_3^+$, K^+, and Na^+, blue-black. These colors may also reflect different degrees of oligomerization in the solid state. The molecules of $NEt_4[Ir(CO)_2(Tcbiim)]$ are dimeric in the solid state. The tetramethylammonium salt may crystallize in discrete trimers or tetramers—salts with smaller cations might oligomerize to an even greater extent. The sodium salt may actually crystallize in chains. X-ray photographs of yellow crystals obtained by layering in a concentrated solution of $Na[Ir(CO)_2(Tcbiim)]$ in acetonitrile with diethyl ether display intense layer lines corresponding to planes separated by approximately 3.2 Å. Subsequent data collection and reduction followed by solution of a Patterson map yielded iridium positions arranged in linear chains with a 3.23-Å metal–metal spacing. Least-squares refinement of these positions resulted in values of R and R_w of 0.396 and 0.640, respectively. Due to disorder in the crystal, the structure failed to refine to a satisfactory R value.

The presence of the dianion of tetracyanobiimidazole in monomeric species of rhodium and iridium is a reflection of its greater acidity as compared to that of the biimidazole ligand. Monomeric complexes of the monoanion of biimidazole are obtained under similar conditions. The presumably planar carbonyl derivatives, $M(CO)_2(Hbiim)$,[4] are potentially analogous structurally to the acetylacetonate complexes, which are known to crystallize in stacks containing metal–metal interactions. $Ir(CO)_2(Hbiim)$ is a highly insoluble black powder. This rather unusual color for an iridium complex, as well as its limited solubility, is presumed to be due to formation of some type of weak metal–metal interaction. The solids of $M(CO)_2(acac)$ are highly anisotropic intrinsic semiconductors.[24] Pressed-pellet measurements on samples of $M(CO)_2(Hbiim)$ and $M'[M(CO)_2(Tcbiim)]$ indicate that these materials are insulators.

Since electron-withdrawing groups such as nitriles have been associated with the stabilization of partially oxidized species, the redox behavior of the salts of $[Ir(CO)_2(Tcbiim)]^-$ was studied. Solutions of $NEt_4[Ir(CO)_2(Tcbiim)]$ are oxidized by Br_2 and I_2. Elemental analysis of the brominated derivative

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suggests simple oxidative addition—1 equiv of Br_2 for each iridium. The presence of four carbonyl stretches in the IR spectra of samples suspended in Nujol or dissolved in methylene chloride implies either isomerization or several mechanisms for oxidative addition. A recent study of the oxidative addition of iodine to rhodium(I) complexes provides evidence for a two-step process in which cis addition of iodine is followed by cis–trans isomerization.[25]

Conclusion

Two important observations stand out regarding this group of compounds. First, there is residual coordinating tendency in some of these monomeric complexes that can lead to pentacoordination, especially for iridium. Second, when pentacoordination does not occur, there is some tendency toward oligomerization of the monomers, especially in the solid state. These results suggest that these ions are good candidates for the preparation of solid materials with extended interactions, including those of mixed valency and highly anisotropic conductivity. We are pursuing this possibility by studying the electrochemical oxidation of concentrated solutions.

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Registry No. $NEt_4[Rh(COD)(Tcbiim)]$, 88179-81-1; $NEt_4[Rh(CO)_2(Tcbiim)]$, 88179-82-2; $NEt_4[Ir(COD)(Tcbiim)]$, 88179-83-3; $C(NH_2)_3[Ir(COD)(Tcbiim)]$, 88179-85-5; $NMe_4[Ir(COD)(Tcbiim)]$, 88179-86-6; $Na[Ir(COD)(Tcbiim)]$, 88179-87-7; $K[Ir(COD)(Tcbiim)]$, 88179-88-8; $NEt_4[Ir(CO)_2(Tcbiim)]$, 83312-49-6; $NMe_4[Ir(CO)_2(Tcbiim)]$, 88157-11-3; $C(NH_2)_3[Ir(CO)_2(Tcbiim)]$, 88199-15-9; $Na[Ir(CO)_2(Tcbiim)]$, 88157-12-4; $K[Ir(CO)_2(Tcbiim)]$, 88157-13-5; $NEt_4[Ir(CO)_2Br_2(Tcbiim)]$, 88199-17-1; $NEt_4[Ir(COD)(PPh_3)(Tcbiim)]\cdot CH_2Cl_2$, 88179-91-3.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, atomic thermal parameters, calculated hydrogen positions, and least-squares planes (27 pages). Ordering information is given on any current masthead page.

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Poly(pyrazolyl)borate Derivatives of Chlorotrimethyltantalum(V). Synthesis, Crystal Structure, and Stereochemically Nonrigid Behavior of Seven-Coordinate Molecules

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The reaction of $TaMe_3Cl_2$ with the poly(pyrazolyl)borate ligands $[RB(pz)_3]^-$ (R = H, pz; pz = pyrazolyl ring) and $[HB(3,5\text{-}Me_2pz)_3]^-$ yields $[RB(pz)_3]TaMe_3Cl$ and $[HB(3,5\text{-}Me_2pz)_3]TaMe_3Cl$, respectively. These new complexes show remarkable stability for alkyltantalum derivatives. An X-ray crystallographic study of $[HB(pz)_3]TaMe_3Cl$ has shown that the solid-state structure of these molecules is a nearly regular capped octahedron with, in this case, a methyl group capping the face formed by the other two methyl groups and the Cl ligand. The monoclinic crystals are in the space group $P2_1/n$ with $a = 9.425$ (6) Å, $b = 12.567$ (5) Å, $c = 14.315$ (5) Å, $\beta = 106.00$ (4)°, $V = 1630$ Å^3, and $Z = 4$. For $[HB(3,5\text{-}Me_2pz)_3]TaMe_3Cl$, this is also the only isomer observed in solution. For the two $[RB(pz)_3]TaMe_3Cl$ complexes, two isomers are observed in solution, one with a Me ligand in the capping position and the other with the Cl ligand in the capping position. These two molecules show stereochemically nonrigid behavior in solution by NMR. The nonequivalent Me ligands for the Me-capped isomer equilibrate above room temperature. Above 86 °C, the two isomers start to interconvert.

Introduction

We have begun a general investigation into the synthesis and characterization of poly(pyrazolyl)borate complexes of Zr, Nb, and Ta. Although this flexible ligand system has been used extensively with other transition metals,[1] only one well-characterized complex of this type has been reported prior to our work. As part of a general investigation into the synthesis of $TaMe_3L_2$ (L = bis chelate, monoanionic ligand) compounds, Wilkinson has reported[2] the synthesis of $[H_2B(pz)_2]_2TaMe_3$ (pz = pyrazolyl ring).

We have previously reported[3,4] the synthesis of $[RB(pz)_3]ZrCl_3$ (R = *i*-Pr, *n*-Bu, H, pz) and $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$. These complexes react with 1 equiv of KO-*t*-Bu to form $[RB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ complexes. In the octahedral structures expected for these butoxide-substituted compounds, two pz rings remain equivalent and one is distinct. This is observed in the ^1H and ^{13}C NMR spectra of $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$. The $[RB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ complexes are fluxional, showing only one type of pz ring at room temperature but quenching to the expected 2:1 pattern at low temperature. Careful study of the $[B(pz)_4]Zr(O\text{-}t\text{-}Bu)Cl_2$ complex allowed us to propose that the mechanism that best explains this dynamic process is a trigonal twist of the $[RB(pz)_3]$ ligand about the Zr–B axis.

We have attempted to extend this chemistry to Ta. The reactions of these ligands with $TaCl_5$ yield complex mixtures that have failed to yield pure $[RB(pz)_3]TaCl_4$ complexes (although mass spectroscopy shows appropriate molecular ion peaks). In contrast, we report here that $[RB(pz)_3]TaMe_3Cl$ complexes readily form, starting with $TaMe_3Cl_2$. These complexes are stable and exhibit, in certain cases, stereochemically nonrigid behavior that is amenable to study by NMR. Although low-valent seven-coordinate complexes are common, few exhibit dynamic behavior that can readily be studied.[5] For the $[RB(pz)_3]TaMe_3Cl$ (R = H, pz) molecules reported here, two isomers are observed in solution at room temperature. Both isomers exhibit dynamic behavior, which is shown to be a different type than the behavior we observed earlier for the six-coordinate $[RB(pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ complexes. We have also carried out a single-crystal X-ray structural analysis of $[HB(pz)_3]TaMe_3Cl$ to verify that the basic structure of these molecules is a capped octahedron.

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