338 *Inorg. Chem.* **1984**, *23*, 338–343

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Complexes of Tetracyanobiimidazole. 1. Dimeric and Tetrameric Species

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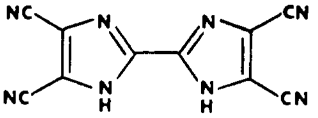
Received June 21, 1983

Complexes of univalent rhodium and iridium with 4,4′,5,5′-tetracyano-2,2′-biimidazole ($H_2Tcbiim$) have been investigated. These compounds always contain the dianion ($Tcbiim^{2-}$) in accord with the greater acidity expected for the cyano-substituted ring system. The dimeric structure of $Ir_2(COD)_2(CH_3CN)(Tcbiim)\cdot CH_3CN$ was confirmed by X-ray crystallography (COD = 1,5-cyclooctadiene). The complex $Ir_2C_{30}H_{30}N_{10}$ crystallizes in the $P\bar{1}$ space group, $Z = 2$ molecules per cell, with $a = 11.699$ (2) Å, $b = 14.043$ (10) Å, $c = 10.127$ (4) Å, $\alpha = 110.87$ (4)°, $\beta = 91.06$ (2)°, and $\gamma = 71.56$ (4)°. A final agreement of $R = 0.037$ was obtained for 2863 observed reflections. The structure shows a unique tridentate bridging by $Tcbiim^{2-}$ due to the unexpected displacement of one coordination site by acetonitrile while the iridium atoms remain four-coordinate. The reactivity of this species was examined with respect to substitution of COD by carbon monoxide, oxidative addition by bromine, and addition of triphenylphosphine. The characterizations of a number of these derivatives for Rh(I) and Ir(I) are described.

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**).



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As we anticipated, the strongly electron-withdrawing cyano substituents profoundly alter the electronic structure compared to that of the parent biimidazole system we investigated earlier.[2-4] The $H_2Tcbiim$ system retains the potential for forming aromatic bridges between pairs of metal ions, however, and it is on such compounds of rhodium(I) and iridium(I) that we now report. We describe herein the preparation, structures, and reactivity patterns of these compounds. In subsequent papers we will describe the behavior of this ligand in forming monomeric species and experiments that pertain to the anisotropic interactions between adjacent planar molecules.

Experimental Section

All syntheses and solution manipulations of rhodium(I) and iridium(I) complexes were performed with Schlenk-type apparatus under prepurified nitrogen. Most reactions were quantitative with absolute yield being limited by recovery losses.

Reagents. Reagents grade aceonitrile was dried by successive distillations.[5] $[M(COD)Cl]_2$,[6] $[M(COD)(OMe)]_2$,[7] M(COD)(acac),[8] $M(CO)_2$(acac),[9] and $H_2Tcbiim$[1] were prepared by methods previously described. All other reagents were used as commercially available without further purification.

Physical Measurements. Infrared spectra (4000–200 cm^{-1}) of samples suspended in KBr pellets, in Nujol mulls placed between NaCl or KBr plates, or in solution were recorded on a Perkin-Elmer Model 1330 grating spectrophotometer.

Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI 49951.

Fourier transform NMR spectra were collected on JEOL FX-90Q and Bruker WM-360 spectrometers. Proton spectra were collected on samples sealed under nitrogen in 5-mm tubes. ^{31}P and ^{13}C spectra of samples in 10-mm tubes were recorded on the JEOL FX-90Q and the Bruker WM-360 using tunable multinuclear probes. All ^1H and ^{13}C resonances are 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.

Preparation of $Rh_2(COD)_2(Tcbiim)$. A mixture of 0.1023 g (0.3298 mmol) of Rh(COD)(acac) and 0.0391 g (0.1670 mmol) of $H_2Tcbiim$ was suspended in 45 mL of 1,2-dichloroethane and heated to reflux for 3 h. As the $H_2Tcbiim$ reacted, the pale yellow suspension slowly became clear and red. This solution was filtered hot and the filtrate cooled at 0 °C overnight. The fine yellow microcrystalline solid that formed was collected by filtration and dried under vacuum. Anal. Calcd for $C_{26}H_{24}N_8Rh_2$: C, 47.73; H, 3.70; N, 17.12. Found: C, 47.70; H, 3.69; N, 17.17. NMR spectra: $^{13}C\{^1H\}$ (CD_3CN) δ 83.4 ($J_{Rh} = 13.7$ Hz), 31.3; ^1H ($CDCl_3$) δ 4.73 (b), 1.87 (b), 2.48 (mult).

Preparation of $Rh_2(COD)_2(Tcbiim)\cdot CH_3CN$. Method A. A mixture of 0.4370 g (0.8862 mmol) of $[Rh(COD)Cl]_2$ and 0.2089 g (0.8862 mmol) of $H_2Tcbiim$ in 45 mL of CH_3CN was heated to reflux for 2 h with formation of a slight precipitate and a yellow solution. The solvent was removed under vacuum and the resulting solid extracted repeatedly with CH_2Cl_2 until extraction yielded a clear solution. The solid was then placed in the thimble of a Soxhlet extractor and heated with hot CH_3CN. Upon cooling, a yellow microcrystalline solid formed, which was isolated by filtration and dried under vacuum. Anal. Calcd for $C_{28}H_{27}N_9Rh_2$: C, 48.36; H, 3.91; N, 18.11. Found: C, 47.99; H, 3.73; N, 18.13.

Method B. A mixture of 0.1017 g (0.4343 mmol) of $H_2Tcbiim$ and 0.2100 g (0.4337 mmol) of $[Rh(COD)OMe]_2$ in 45 mL of MeOH was heated to reflux for 3 h with formation of a yellow solid and orange solution. After cooling, the solution was concentrated to one-third volume under reduced pressure. The solid was then collected by filtration and dried under vacuum. Recrystallization from CH_3CN yields a solid that was identified as $Rh_2(COD)_2(CH_3CN)(Tcbiim)$ by comparison of its infrared spectrum with that of an authentic sample.

Method C. A mixture of 0.2894 g (0.9330 mmol) of Rh(COD)(acac) and 0.1093 g (0.4667 mmol) of $H_2Tcbiim$ in 25 mL of MeOH was heated to reflux for 3 h with formation of a yellow solid. Subsequent workup as previously described yielded the product, $Rh_2(COD)_2(CH_3CN)(Tcbiim)$.

Preparation of $Rh_4(CO)_8(Tcbiim)_2$. Carbon monoxide was passed through a suspension of 58 mg (0.0886 mmol) of $Rh_2(COD)_2(Tcbiim)$ in 20 mL of CH_2Cl_2 for 20 min. After 10 min the starting material had reacted, forming a clear red solution. Slowly an orange solid formed. The solution was concentrated under a stream of nitrogen and the bright orange microcrystalline solid collected by filtration. (The solvates of the dimer function equally well as starting materials for the generation of this tetramer.) Anal. Calcd for $C_{28}N_{16}O_8Rh_4$: C, 30.57; H. 0.00; N, 20.37. Found: C, 30.37; H, 0.06; N, 20.23.

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

[3] Kaiser, S. W.; Saillant, R. B.; Butler, W. M.; Rasmussen, P. G. *Inorg. Chem.* **1976**, *15*, 2681.

[4] Kaiser, S. W.; Saillant, R. B.; Butler, W. M.; Rasmussen, P. G. *Inorg. Chem.* **1976**, *15*, 2688.

[5] Gordon, A. J.; Ford, R. A. "The Chemists Companion"; Wiley: New York, 1972.

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

[7] (a) Chatt, G.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 4735. (b) Robinson, S. D.; Shaw, B. L. *J. Chem. Soc.* **1965**, 4997.

[8] Rhodium and iridium complexes were prepared by the method of Robinson and Shaw cited in ref 7b by replacing $[M(COD)HCl_2]_2$ and Na_2CO_3 with $[M(COD)Cl]_2$.

[9] (a) Bonati, F.; Wilkinson, G. *J. Chem. Soc.* **1964**, 3156. (b) Bonati, F.; Ugo, R. *Chim. Ind.* (*Milan*) **1964**, *46*, 1486.

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Preparation of $Ir_2(COD)_2(CH_3CN)(Tcbiim)\cdot CH_3CN$ (2). A mixture of 0.1554 g (0.3890 mmol) of Ir(COD)(acac) and 0.0458 g (0.1956 mmol) of H_2Tcbiim in 20 mL of CH_3CN was heated to reflux for 1 h. After 15 min of heating, a clear orange solution had formed, which upon cooling yielded only a slight precipitate. The volume was reduced by half under vacuum with the formation of an orange microcrystalline solid. Recrystallization from CH_3CN yielded the pure product. Anal. Calcd for $C_{30}H_{30}N_{10}Ir_2$: C, 39.38; H, 3.30; N, 15.31. Found: C, 39.51; H, 3.39; N, 15.24.

Preparation of $Ir_2(COD)_2(PPh_3)_2(Tcbiim)$ (3). A solution of 0.1161 g (0.4426 mmol) of triphenylphosphine in 10 mL of CH_2Cl_2 was added dropwise with stirring to 0.1005 g (0.1098 mmol) of $Ir_2(COD)_2(CH_3CN)(Tcbiim)\cdot CH_3CN$ dissolved in 80 mL of CH_2Cl_2. Within minutes the orange microcrystalline product began to form. The solid was isolated by filtration and dried under vacuum. Anal. Calcd for $C_{62}H_{54}N_8P_2Ir_2$: C, 54.86; H, 4.01; N, 8.25; P, 4.56. Found: C, 53.98; H, 4.05; N, 8.44; P, 4.63.

Preparation of $Ir_4(CO)_8(Tcbiim)_2$ (4). Method A. Carbon monoxide was passed through a suspension of 70 mg (0.0765 mmol) of $Ir_2(COD)_2(CH_3CN)(Tcbiim)\cdot CH_3CN$ in 15 mL of CH_2Cl_2 for 15 min. After 10 min the starting metal complex had reacted, forming a deep purple solution. Gradually a dark solid precipitated. The solution was concentrated under a stream of nitrogen and the dark reddish brown microcrystalline solid collected by filtration. Anal. Calcd for $C_{28}N_{16}O_8Ir_4$: C, 23.08; H, 0.00; N, 15.38. Found: C, 23.32; H, 0.26; N, 15.17.

Method B. A suspension of 8.5 mg (0.0363 mmol) of H_2Tcbiim in 10 mL of CH_2Cl_2 containing 25.3 mg (0.0728 mmol) of $Ir(CO)_2$(acac) was stirred for 1 h. As the H_2Tcbiim reacted, the solution slowly became purple followed by precipitation of a dark solid. The solid was isolated by filtration and shown to be $Ir_4(CO)_8(Tcbiim)_2$ by comparison of its infrared spectrum with that of an authentic sample.

Preparation of $Ir_4(CO)_4(PPh_3)_4(Tcbiim)_2$ (5). To a suspension of 0.2059 g (0.1413 mmol) of $Ir_4(CO)_8(Tcbiim)_2$ in 80 mL of CH_2Cl_2 was added dropwise a solution of 0.1482 g (0.5650 mmol) of PPh_3 in 10 mL of CH_2Cl_2. The suspension was stirred 8 h at room temperature, yielding a clear red solution. The volume was reduced to several milliliters under vacuum and then layered with 5 mL of hexane. A bright yellow crystalline solid formed over a period of 2 weeks. Anal. Calcd for $C_{96}H_{60}N_{16}O_4P_4Ir_4$: C, 48.18; H, 2.53; N, 9.36; P, 5.17. Found: C, 48.04; H, 2.49; N, 9.29; P, 5.23. NMR spectra ($CDCl_3$): ^{31}P δ 26.2; $^{13}C\{^1H\}$ δ 169.5, 134.2 t, $|J_{PC} + J_{P'C}| = 24.4$ Hz, 131.4, 129.9 t, $|J_{PC} + J_{P'C}| = 53.0$ Hz, 128.7 t, $|J_{PC} + J_{P'C}| = 10.8$ Hz.

Preparation of $Ir_2(COD)_2Br_4(Tcbiim)$ (6). Several drops of bromine were dissolved in 5 mL of CH_2Cl_2 and added dropwise to a solution of 96 mg (0.1049 mmol) of $Ir_2(COD)_2(CH_3CN)(Tcbiim)\cdot CH_3CN$ in 40 mL of CH_2Cl_2. Immediately a pale yellow solid began to form, which was isolated by filtration, rinsed with CH_2Cl_2, and dried under vacuum. Anal. Calcd for $C_{26}H_{24}N_8Br_4Ir_2$: C, 27.10; H, 2.10; N, 9.72; Br, 27.73. Found: C, 26.96; H, 2.06; N, 9.63; Br, 27.84.

Crystal Structure Determination of $Ir_2(COD)_2(CH_3CN)(Tcbiim)\cdot CH_3CN$. Data Collection and Reduction. Single crystals of $Ir_2(COD)_2(CH_3CN)(Tcbiim)\cdot CH_3CN$ were grown by the slow evaporation of a saturated solution of the complex in acetonitrile using nitrogen as the flow gas. A small well-formed, sword-shaped yellow crystal was attached to the outside of the tip of a fine glass fiber and mounted on a Syntex $P\bar{1}$ four-circle diffractometer. Au automatic centering routine carried out on 15 reflections yielded cell parameters conforming to the acentric $P1$ or centric $P\bar{1}$ space group. Axial photographs showed no mirror to be present. Intensity data were collected with use of the θ–2θ scan technique and reduced with use of methods previously described.[10] Only those data for which $F^2 \geq 3\sigma(F^2)$ were used subsequently. A summary of crystallographic data is presented in Table I.

Table I. Crystallographic Parameters for $Ir_2(COD)_2(CH_3CN)(Tcbiim)\cdot CH_3CN$

space group	$P\bar{1}$
a, Å	11.699 (2)
b, Å	14.043 (10)
c, Å	10.127 (4)
α, deg	110.87 (4)
β, deg	91.06 (2)
γ, deg	71.56 (4)
V, Å^3	1466 (1)
mol wt	915.1
Z	2
d_{calcd}, g/cm^3	2.070
cryst dimens, mm	0.078–0.046
cryst shape	swordlike
radiation, Å	λ(Mo Kα) 0.71069, monochromatized from graphite cryst
linear abs coeff, μ(Mo Kα), cm^{-1}	90.708
transmission factors	0.49–0.66
scan speed, deg/min	variable, 2.5–12, determined as a function of peak intens
ratio of background to peak scan time	0.8
std reflcns	(410), (121), (102)
% dev of stds during data collection	2
2θ limit, deg	50
reflcns collected	4105
reflcns with $F^2 \geq 3\sigma(F^2)$	2863

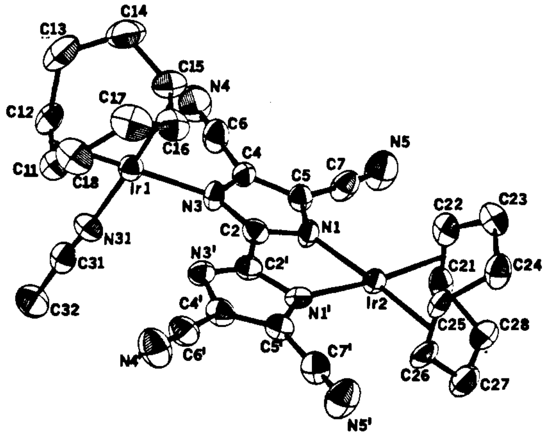

Figure 1. Structure of $Ir_2(COD)_2(CH_3CN)(Tcbiim)$.

Solution and Refinement of the Structure. This structure was solved by conventional Patterson and Fourier syntheses. Several cycles of full-matrix least-squares refinement led to isotropic convergence at $R = 0.050$ and $R_w = 0.061$. Continued refinement using anisotropic thermal parameters for atoms led to convergence with values of 0.040 and 0.048 for $R = R_w$, respectively. Idealized hydrogen atom coordinates were calculated and isotropic temperature factors set such that $B_H = B_C + 1$ where C is the carbon atom to which H is bonded. Two additional cycles of refinement using the corrected data, as well as the correction for the anomalous scatterers, led to a final convergence with $R = 0.037$ and $R_w = 0.045$. In the final difference map, four peaks near the iridium atoms of approximately 3.9 e Å^{-3} were observed. No other peak was greater than 1.13 e Å^{-3}.

Description of the Structure

A labeled representation of the molecular structure of $Ir_2(COD)_2(CH_3CN)(Tcbiim)\cdot CH_3CN$ is displayed in Figure 1. A view of the unit cell has not been included since no significant packing interactions are evident between either the dimeric complexes or the acetonitrile of crystallization. The asymmetric unit consists of the molecular dimer, as well as a molecule of solvated acetonitrile. The unit cell is composed

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[10] Computer programs used during the structural analysis were SYNCOR (data reduction by W. Shmonsees), FORDAP (Fourier synthesis by A. Zalkin), ORFLS (full-matrix least-squares refinement by Busing, Martin, and Levy), ORFFE (distances, angles, and their esdαpos 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.; Waber, 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 II. Interatomic Distances (Å, with Esd's) for $Ir_2(COD)_2(CH_3CN)(Tcbiim)\cdot CH_3CN$

(A) Distances from the Iridium Atoms

Ir1–N3	2.087 (10)	Ir2–N1	2.094 (10)
Ir1–N3′	3.366 (11)	Ir2–N1′	2.080 (10)
Ir1–N31	2.044 (12)	Ir2–C21	2.128 (14)
Ir1–C11	2.118 (14)	Ir2–C22	2.115 (13)
Ir1–C12	2.147 (13)	Ir2–C25	2.118 (13)
Ir1–C15	2.142 (14)	Ir2–C26	2.092 (13)
Ir1–C16	2.124 (14)	Ir2–M21	2.000
Ir1–M11	2.014	Ir2–M22	1.984
Ir1–M12	2.018	Ir1–Ir2	5.993

(B) Distances within the Tcbiim^{2-} Ligand

N1–C2	1.334 (16)	N1′–C2′	1.348 (16)
C2–N3	1.344 (16)	C2′–N3′	1.299 (16)
N3–C4	1.382 (16)	N3′–C4′	1.358 (17)
C4–C5	1.365 (18)	C4′–C5′	1.373 (19)
C5–N1	1.373 (16)	C5′–N1′	1.369 (16)
C4–C6	1.425 (20)	C4′–C6′	1.420 (20)
C5–C7	1.390 (20)	C5′–C7′	1.441 (20)
C6–N4	1.143 (18)	C6′–N4′	1.134 (18)
C7–N5	1.163 (18)	C7′–N5′	1.136 (18)
N1–N1′	2.632 (14)	N3–N3′	3.096 (15)
C2–C2′	1.473 (17)		

(C) Distances within the C_8H_{12} Ligands

COD 1		COD 2	
C11–C12	1.402 (20)	C21–C22	1.417 (20)
C12–C13	1.518 (23)	C22–C23	1.520 (20)
C13–C14	1.514 (25)	C23–C24	1.536 (20)
C14–C15	1.490 (22)	C24–C25	1.498 (20)
C15–C16	1.383 (21)	C25–C26	1.409 (20)
C16–C17	1.515 (22)	C26–C27	1.479 (20)
C17–C18	1.493 (23)	C27–C28	1.529 (21)
C18–C11	1.513 (21)	C28–C21	1.501 (20)

(D) Distances within the CH_3CN Ligand

C31–C32	1.477 (21)	N31–C31	1.099 (17)

(E) Distances within the CH_3CN Solvate

C41–C42	1.427 (34)	N41–C41	1.130 (31)

of two such species, the second being generated by the inversion center. Table II and III contain pertinent bond lengths and angles.

The coordination about each iridium atom can be described as square planar. The square plane about Ir1 consists of nitrogen N3 of the Tcbiim^{2-} ligand, nitrogen N31 of the coordinated acetonitrile, and midpoints M11 (C11–C12) and M12 (C15–C16) of the olefinic groups of a cyclooctadiene ligand. None of these deviate more than 0.062 Å from their best least-squares plane. The square plane about Ir2 consists of nitrogens N1 and N1′ of the Tcbiim^{2-} ligand, as well as olefinic midpoints M21 (C21–C22) and M22 (C25–C26) of the second cyclooctadiene ligand. None of these positions deviate more than 0.047 Å from their best least-squares plane. These two square coordination planes are nearly perpendicular to one another with a dihedral angle of 96.9° between the normals to each plane.

The angles about Ir1 deviate only slightly from idealized square-planar geometry. The greatest deviation arises from the M11–Ir–M12 angle (88.2°) containing the midpoints of the olefin bonds of cyclooctadiene. This imposed angle due to the bite of this ligand is in the range normal for other COD complexes.[11] The remaining angles about Ir1 (N3–Ir1–N31 = 90.8 (4)°, N31–Ir1–M11 = 91.0°, and M12–Ir1–N3 = 90.1°) compensate for the distortion created by the metal–olefin bonding geometry.

Table III. Interatomic Angles (deg) for $Ir_2(COD)_2(CH_3CN)(Tcbiim)\cdot CH_3CN$

(A) Angles about the Iridium Atoms

	Ir1		
N3–Ir1–N31	90.8 (4)	N31–Ir1–M11	91.0
M11–Ir1–M12	88.2	M12–Ir1–N3	90.1
N3–Ir1–M11	177.1	N31–Ir1–M12	175.8
	Ir2		
N1–Ir2–N1′	78.2 (4)	N1′–Ir2–M22	97.8
M22–Ir2–M21	87.1	M21–Ir2–N1	97.1
M22–Ir2–N1	175.8	N1′–Ir2–M21	173.9

(B) Angles within the Tcbiim^{2-} Ligand

C2–N1–C5	104.1 (10)	C2′–N1′–C5′	101.2 (10)
N3–C2–N1	115.0 (11)	N3′–C2′–N1′	118.1 (11)
N3–C2–C2′	127.9 (12)	N3′–C2′–C2	127.8 (12)
N1–C2–C2′	117.1 (12)	N1′–C2′–C2	114.2 (11)
C4–N3–C2	103.0 (10)	C4′–N3′–C2′	102.3 (11)
N3–C4–C5	109.3 (11)	N3′–C4′–C5′	109.7 (11)
N3–C4–C6	122.5 (11)	N3′–C4′–C6′	123.0 (13)
C6–C4–C5	128.2 (12)	C6′–C4′–C5′	127.2 (13)
C4–C5–N1	108.5 (11)	C4′–C5′–N1′	108.7 (11)
C4–C5–C7	126.8 (13)	C4′–C5′–C7′	126.8 (13)
N1–C5–C7	124.5 (12)	N1′–C5′–C7′	124.5 (12)
C4–C6–N4	177.3 (17)	C4′–C6′–N4′	177.9 (19)
C5–C7–N5	174.5 (17)	C5′–C7′–N5′	175.5 (17)

(C) Angles within the C_8H_{12} Ligands

COD 1		COD 2	
C18–C11–C12	125.1 (13)	C28–C21–C22	123.4 (13)
C11–C12–C13	123.6 (14)	C21–C22–C23	123.3 (13)
C12–C13–C14	114.9 (13)	C22–C23–C24	112.5 (12)
C13–C14–C15	113.2 (14)	C23–C24–C25	112.1 (11)
C14–C15–C16	127.2 (15)	C24–C25–C26	123.0 (13)
C15–C16–C17	123.6 (15)	C25–C26–C27	122.9 (13)
C16–C17–C18	114.6 (13)	C26–C27–C28	113.3 (12)
C17–C18–C11	114.4 (13)	C27–C28–C29	111.8 (12)

(D) Angle within the CH_3CN Ligand

N31–C31–C32	176.7 (16)

(E) Angle within the CH_3CN Solvate

N41–C41–C42	173.5 (32)

The bite of the tetracyanobiimidazole dianion introduces a marked deviation from square geometry about Ir2. This N1–Ir2–N1′ angle of 78.2 (4°), while only slightly affecting the bite of the trans COD ligand (M21–Ir2–M22 = 87.1°), induces a large distortion in the other angles of the square plane (N1–Ir2–M21 = 97.1°; N1′–Ir2–M22 = 97.8°).

The bite angles observed in other complexes of biimidazole and its derivatives range from 75.3° in $NEt_4[Ir(COD)(PPh_3)(Tcbiim)]\cdot CH_2Cl_2$[12] to 82.78 (10)° in $[Cu_2(Me_5dien)_2(biim)](BPh_4)_2$.[13] Differences in this angle arise from the multiplicity of bonding modes of this type of ligand.

In this complex the Tcbiim^{2-} ligand functions as a planar tridentate bridge by coordinating to the two iridium atoms through three of its four ring nitrogen atoms. All Ir–N bond lengths are equal within experimental error (Ir1–N3, 2.087 (10) Å; Ir2–N1, 2.094 (10) Å; Ir2–N1′, 2.080 (10) Å). The distance of 3.366 (11) Å between Ir1 and N3′ is well outside of the range of Ir–N bond lengths (2.02–2.25 Å),[14] clearly showing the absence of interaction between these atoms. Ir–N bond lengths of 2.322 (15) and 2.116 (13) Å have been observed for the dianion of tetracyanobiimidazole as reported for $NEt_4[Ir(COD)(PPh_3)(Tcbiim)]$.[12]

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[11] (a) Churchill, M. R.; Bezman, S. A. *Inorg. Chem.* **1973**, *12*, 260. (b) Churchill, M. R.; Benzman, S. A. *Ibid.* **1972**, *11*, 2243. (c) Coetzer, J.; Gafner, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 985. (d) Ibers, J. A.; Snyder, R. G. *Acta Crystallogr.* **1962**, *15*, 923.

[12] Rasmussen, P. G.; Bailey, O. H.; Bayôn, J. C.; Butler, W. M. *Inorg. Chem.*, following paper in this issue.

[13] Haddad, M. S.; Duesler, E. N.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 141.

[14] (a) Ricci, J. S.; Ibers, J. A.; Fraser, M. S.; Baddley, W. H. *J. Am. Chem. Soc.* **1970**, *92*, 3489. (b) Bresciani-Pahor, N.; Calligaris, M.; Nardin, G.; Delise, P. *J. Chem. Soc., Dalton Trans.* **1976**, 762.

Table IV. Fractional Atomic Coordinates for $Ir_2(COD)_2(CH_3CN)(Tcbiim)\cdot CH_3CN$

atom	x	y	z
Ir1	0.07360 (5)	0.19475 (4)	0.80274 (5)
Ir2	0.46115 (4)	−0.21806 (4)	0.45741 (5)
N1	0.3527 (9)	−0.1144 (8)	0.6483 (11)
C2	0.2891 (12)	−0.0167 (10)	0.6495 (13)
N3	0.2096 (9)	0.0469 (8)	0.7652 (11)
C4	0.2267 (11)	−0.0166 (10)	0.8461 (14)
C5	0.3144 (12)	−0.1135 (10)	0.7764 (14)
C6	0.1626 (14)	0.0207 (11)	0.9830 (17)
C7	0.3550 (13)	−0.2004 (12)	0.8207 (15)
N4	0.1091 (14)	0.0475 (11)	1.0907 (15)
N5	0.3793 (14)	−0.2727 (12)	0.8588 (15)
N1′	0.3966 (9)	−0.0733 (8)	0.4239 (11)
C2′	0.3134 (12)	0.0085 (11)	0.5258 (14)
N3′	0.2643 (10)	0.0982 (9)	0.5050 (12)
C4′	0.3222 (13)	0.0770 (11)	0.3775 (15)
C5′	0.4023 (12)	−0.0267 (11)	0.3274 (14)
C6′	0.2957 (14)	0.1520 (12)	0.3079 (16)
C7′	0.4812 (14)	−0.0796 (12)	0.1964 (17)
N4′	0.2782 (14)	0.2115 (12)	0.2521 (16)
N5′	0.5376 (13)	−0.1178 (12)	0.0891 (16)
C11	−0.0279 (13)	0.3374 (12)	0.7702 (16)
C12	−0.0874 (12)	0.3331 (11)	0.8858 (16)
C13	−0.2000 (15)	0.3004 (15)	0.8765 (19)
C14	−0.1759 (15)	0.1803 (15)	0.8327 (21)
C15	−0.0570 (13)	0.1130 (13)	0.7462 (16)
C16	−0.0118 (14)	0.1212 (13)	0.6270 (16)
C17	−0.0814 (16)	0.2007 (15)	0.5609 (18)
C18	−0.0651 (16)	0.3088 (14)	0.6209 (18)
C21	0.5607 (14)	−0.3456 (11)	0.5240 (14)
C22	0.4509 (13)	−0.3606 (11)	0.4758 (15)
C23	0.4442 (13)	−0.4428 (11)	0.3323 (15)
C24	0.5106 (14)	−0.4347 (12)	0.2094 (15)
C25	0.5150 (12)	−0.3232 (10)	0.2425 (14)
C26	0.6116 (13)	−0.2902 (11)	0.3046 (15)
C27	0.7174 (14)	−0.3626 (13)	0.3434 (17)
C28	0.6826 (12)	−0.4126 (12)	0.4414 (17)
N31	0.1755 (10)	0.2751 (9)	0.9336 (13)
C31	0.2261 (13)	0.3218 (11)	1.0064 (15)
C32	0.3006 (14)	0.3793 (13)	1.1002 (16)
N41	0.0294 (25)	0.4506 (23)	0.3053 (34)
C41	−0.0110 (24)	0.3841 (20)	0.2855 (27)
C42	−0.0704 (28)	0.3051 (21)	0.2503 (29)

The tetracyanobiimidazolato ligand is essentially planar. Least-squares planes calculated for each ring of the substituted biimidazole show no atom to deviate more than 0.054 Å from its respective plane. The dihedral angle between the normals to the imidazolato rings is 1.0°. Dihedral angles between the rings of other biimidazole ligands have ranged from 0 to 5.2°.[3,15]

While the coordinated ring nitrogen atoms clearly lie within their metal's coordination plane, the tetracyanobiimidazole ligand does not lie within either of these planes. The plane of the ligand is tilted approximately 7° out of the plane containing Ir2 and the bidentate portion of the $Tcbiim^{2-}$. Without the constraint imposed by a bidentate linkage to $Tcbiim^{2-}$, the coordination plane about Ir1 is theoretically free to make any angle with the plane of this ligand. The observed dihedral angles are 96.0 and 97.0° between each of the two imidazolato rings and the Ir1 coordination plane.

Bond angles and distances within the dianion of tetracyanobiimidazole compare well with the corresponding parameters reported for other complexes of the dianions of biimidazole[3,4,13] and tetracyanobiimidazole.[12]

Both 1,5-cyclooctadiene ligands are found in the normal "tub" conformation. The least-squares planes containing the four olefinic carbon atoms of each COD ligand (C11, C12, C15, C16; C21, C22, C25, C26) are nearly perpendicular to their respective metal's coordination plane (89.2 and 88.8°). Deviation of these atoms from their least-squares plane indicates that each olefinic group within a COD ligand is twisted slightly relative to one another. This type of behavior is common.

Carbon–carbon bond lengths for the olefins range from 1.383 (21) to 1.409 (20) Å. The bond lengths about Ir2 (Ir2–M21 = 2.000 Å; Ir2–M22 = 1.984 Å) are slightly shorter than those about Ir1 (Ir1–M11 = 2.014 Å; Ir1–M12 = 2.018 Å). All are typical for COD bonded to heavy-metal atoms, as in the range of single-bond C–C distances of 1.479 (20)–1.536 (20) Å.[11b]

The coordinated acetonitrile is σ-bonded through nitrogen N31 to Ir1 with a bond length of 2.044 (12) Å. The CH_3CN molecule is tipped slightly out of the coordination plane as evidenced by the perpendicular distances of atoms C31 and C32 from this least-squares plane.

Pt–N bond lengths of coordinated nitriles range from 1.95 to 2.04 Å, although in some of these systems the nitrile is part of a larger chelating ligand.[16] A metal–nitrogen bond length of 2.152 (7) Å has been reported in a rhodium(II) dimer containing coordinated acetonitrile.[17]

Results

$H_2Tcbiim$ reacts with rhodium dimers bridged by anionic ligands to yield dinuclear complexes containing the dianion of tetracyanobiimidazole. Unlike biimidazole, which requires strongly basic bridging ligands such as methoxide to remove its pyrrole-like ring hydrogens, tetracyanobiimidazole can displace the chloride bridges of $[Rh(COD)Cl]_2$ to form $Rh_2(COD)_2(Tcbiim)$ while liberating HCl. The methoxy-bridged dimer $[Rh(COD)(OMe)]_2$ reacts with $H_2Tcbiim$ in a similar fashion. Dimer is also isolated upon heating solutions of Rh(COD)(acac) and tetracyanobiimidazole. All form dimers regardless of the ratio of metal to ligand—the driving force being the insolubility of $Rh_2(COD)_2(Tcbiim)$.

$Rh_2(COD)_2(Tcbiim)$ shows a strong tendency to solvate when prepared or crystallized from coordinating solvents such as acetone or acetonitrile. This solvent can be removed by refluxing in a high boiling solvent such as 1,2-dichloroethane although the process is slow due to limited solubility in this medium.

Ir(COD)(acac) reacts with $H_2Tcbiim$ in acetonitrile to yield the solvated dimer $Ir_2(COD)_2(Tcbiim)\cdot 2CH_3CN$. Reactions of $H_2Tcbiim$ with $[Ir(COD)Cl]_2$ or $[Ir(COD)(OMe)]_2$ result in the formation of insoluble pink solids of uncertain composition. Infrared spectra indicate complexation of $Tcbiim^{2-}$. Elemental analysis is suggestive of dimer formation.

Infrared spectral data for the rhodium dimers $Rh_2(COD)_2(Tcbiim)$ and $Rh_2(COD)_2(Tcbiim)\cdot$(solvate) suggest that these species are very similar. The spectra differ only where bands associated with solvated acetone (1700 cm^{-1}, $\nu_{C=O}$) or acetonitrile (750 cm^{-1}) are observed. We did not observe bands typical of the C=C stretching bands of uncoordinated asymmetrical olefins, which are normally observed near 1650 cm^{-1}.[18]

The ^1H NMR spectrum of $Rh_2(COD)_2(Tcbiim)$ has two broad multiplets attributed to the methylene protons and a single peak due to the olefinic protons, which integrate in a 1:1:1 ratio as expected for equivalent COD ligands. The reasonances of the methylene protons are normal compared

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(15) Dance, I. G.; Abushamleh, A. S.; Goodwin, H. A. *Inorg. Chim. Acta* **1980**, *43*, 217.

(16) (a) Schwarzenbach, D.; Pinkerton, A.; Chapuis, G.; Wenger, J.; Ros, R.; Roulet, R. *Inorg. Chim. Acta* **1977**, *25*, 255. (b) Beck, W.; Keubler, M.; Leidl, E.; Nagel, U.; Schaal, M.; Cenini, S.; Del Buttero, P.; Licandro, E.; Maiorani, S. *J. Chem. Soc., Chem. Commun.* **1981**, 446. (c) Lauher, J. W.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 640.

(17) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1981**, *20*, 584.

(18) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed.; Wiley-Interscience: New York, 1970.

to those of COD ligands in other rhodium(I) complexes. The olefinic peak is downfield relative to the range found for COD trans to Schiff base ligands.[19]

Proton-decoupled ^{13}C NMR supplies additional evidence for the equivalence of the cyclooctadienyl ligands. The sharp singlet at 31.3 ppm is near the reported value of 28.3 ppm for the methylene carbons of the free ligand.[20] The resonance of the olefinic carbons (83.4 ppm) is shifted significantly from that of the free ligand (128.7 ppm). This chemical shift, as well as the Rh–C coupling constant of 13.7 Hz, are in the normal range for π-bonded olefins in square-planar complexes of rhodium.[19]

X-ray analysis of the biimidazolato analogue $Rh_2(COD)_2(biim)$ indicates the presence of symmetrically bridged planar dimers in the solid state.[3] Structurally similar dimers are proposed for $Rh_2(COD)_2(Tcbiim)$. Infrared and nuclear magnetic data are consistent with this assignment.

The infrared spectrum of $Ir_2(COD)_2(CH_3CN)(Tcbiim)\cdot CH_3CN$ reflects the reduced symmetry of this dimer relative to $Rh_2(COD)_2(Tcbiim)\cdot CH_3CN$ and $[Ir(COD)Cl]_2$. Two weak absorbances at 2318 and 2291 cm^{-1} in the spectrum of the iridium complex result from the vibration of the C≡N triple bond of the acetonitrile. In the rhodium spectrum this stretch cannot be resolved. A small splitting is observed in the absorbance associated with the nitriles to $Tcbiim^{2-}$ in both of these species.

In general, the strongest bands observed for $Rh_2(COD)_2(Tcbiim)$ are shifted slightly but are present in the spectrum of $Ir(COD)_2(CH_3CN)(Tcbiim)$. Absorbances due to the COD ligands compare well with those observed in $[Ir(COD)Cl]_2$. These peaks tend to show more structure in the $Tcbiim^{2-}$ spectrum. These subtle distinctions may be an effect created by differences in the local symmetries of the ligands in these closedly related species.

Proton NMR indicated structural differences between $Rh_2(COD)_2(biim)$ and $Ir_2(COD)_2(biim)$.[21] At the time of that work, these differences were attributed to probable solvent association. In light of this work, this explanation seems very likely.

Iridium dimers are clearly more susceptible to bridge asymmetries than their rhodium counterparts. This may be a result of iridium's greater tendency to increase its coordination number. Solutions of $Ir_2(COD)_2(CH_3CN)(Tcbiim)$ in methylene chloride react with excess triphenylphosphine to yield an orange microcrystalline solid with stoichiometry $Ir_2(COD)_2(PPh_3)_2(Tcbiim)$. PPh_3 displaces COD ligands in the biimidazolato-bridged dimer $Rh_2(COD)_2(biim)$.[21]

Infrared spectral data are consistent with the presence of chelating COD ligands. Bands near 1650 cm^{-1} associated with uncomplexed olefins are not observed. The splitting observed in the absorbance due to the $Tcbiim^{2-}$ nitriles is also consistent with a tetracyanobiimidazolato ligand bridging two pentacoordinate iridium atoms. A similar pentacoordinate geometry has been found for the iridium monomer $NEt_4[Ir(COD)(PPh_3)(Tcbiim)]$;[12] however, other structural possibilities cannot be ruled out completely.

Solutions of $Ir_2(COD)_2(CH_3CN)(Tcbiim)$ also react with bromine to yield a pale yellow solid that possesses 2 mol of Br_2/dimeric unit. Since iridium(III) is normally octahedrally coordinated, a structure containing a symmetrically bridged tetradentate $Tcbiim^{2-}$ is proposed.

Carbon monoxide readily displaces the cyclooctadienyl ligands of dimers of rhodium(I) and iridium(I) containing the dianion of tetracyanobiimidazole. $Rh_2(COD)_2(Tcbiim)$ or any of its solvates reacts rapidly when CO is bubbled through suspensions of the complex in methylene chloride. Upon reaction, the solid is drawn into solution with a bright orange microcrystalline solid forming shortly thereafter. $Ir_2(COD)_2(CH_3CN)(Tcbiim)$ reacts similarly to yield a reddish brown microcrystalline solid.

Reactions of $H_2Tcbiim$ with $M(CO)_2(acac)$ also result in formation of the species described above. While this method is more direct, displacment of the COD ligands has proven to be the best method for obtaining product of high purity.

The solid-state infrared spectra of these iridium and rhodium carbonyl derivatives are essentially identical except for the positions of the carbonyl stretches. The carbonyl stretches for the rhodium complex range from 2035 to 2117 cm^{-1} while those of the iridium complex are observed between 2026 and 2116 cm^{-1}.

$Rh_2(COD)_2(biim)$ and $Ir_2(COD)_2(biim)$ react with carbon monoxide under conditions identical with those of the tetracyanobiimidazolato analogues to yield solids that exhibit similar patterns in the carbonyl region of the infrared spectrum.[21] A tetranuclear configuration was determined by X-ray crystal analysis for the rhodium derivative.[4] A similar structure is proposed for the carbonyl derivatives of rhodium and iridium dimers containing tetracyanobiimidazole.

The tetracyanobiimidazolato-bridged tetramer reacts with 4 equiv of triphenylphosphine to yield a yellow crystalline complex containing a mixture of ligands. Elemental analysis is consistent with the formulation $Ir_4(CO)_4(PPh_3)_4(Tcbiim)_2$. The solid-state infrared spectrum exhibits one sharp and one broad absorbance at 2091 and 2023 cm^{-1}, respectively. In solution three absorbances at 2088, 2023, and 1990 cm^{-1} are observed.

Not all the resonances of the tetracyanobiimidazolato ligands could be identified in the $^{13}C\{^1H\}$ NMR spectrum of this complex. Only one weak singlet is observed in the region where the carbons of $Tcbiim^{2-}$ are normally found (119.9 ppm). A singlet at 169.5 ppm has been assigned to the carbonyl ligands of this complex. The resonances of greatest intensity are those associated with the phenyl rings of the phosphine ligand. Triplets are observed for the ortho and meta carbons while the para and phosphorus-bonded carbons appear as sharp and broad singlets, respectively. A singlet at 26.2 ppm is observed in the ^{31}P spectrum. The infrared and NMR data are consistent with replacement of the carbonyls attached to the terminal iridium atoms by phosphine ligands.

The structurally analogous carbonyl tetramers of biimidazole and tetracyanobiimidazole provide an opportunity to compare the π-acceptor abilities of these closely related ligands. Carbonyl stretching frequencies in transition-metal complexes have been related to the extent of π^* donation—an effect which is dependent upon the ligands trans to a *cis*-dicarbonyl in square-planar coordination geometry.[22]

The CO absorbances of $Rh_4(CO)_8(biim)_2$ and $Ir_4(CO)_8(biim)_2$ range from 2080 to 2010 and 2068 to 2000 cm^{-1}, respectively.[21] Those of the tetracyanobiimidazole derivatives are observed from 2117 to 2035 and 2116 to 2026 cm^{-1}, respectively. The shift in average carbonyl stretching frequency of over 30 cm^{-1} reflects a significant increase in the ability of the cyano-substituted biimidazole to accept d-electron density via its lower lying π^* orbitals. The mean carbonyl stretching frequencies of $M(CO)_2(acac)$ complexes increase only 10 cm^{-1} upon substitution of CF_3 groups for the methyl groups of the acetylacetonato ligand.[23] As in the case of the tetrameters of biimidazole, conductivities measured on pressed-pellet

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(19) Platzer, N.; Goasdoue, N.; Bonnaire, R. *J. Organomet. Chem.* **1978**, *160*, 455.

(20) Proton and Carbon-13 NMR Collections, Sadtler Research Laboratories, 1980.

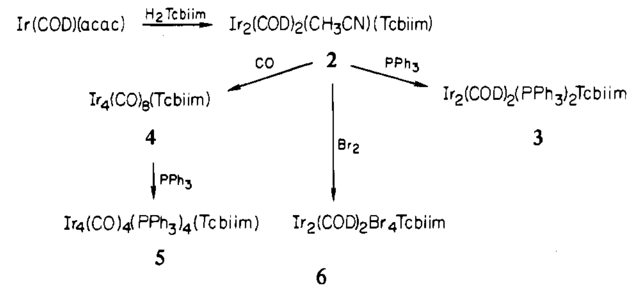
(21) Kaiser, S. W. Dissertation, University of Michigan, 1975.

(22) Bresler, L. S.; Buzina, N. A.; Varshavskyu, Y. S.; Kiseleva, N. V.; Cherkasova, T. G. *J. Organomet. Chem.* **1979**, *171*, 229.

(23) Bonati, F.; Ugo, R. *J. Organomet. Chem.* **1968**, *11*, 341.

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.

Acknowledgment. J.C.B. wishes to thank the Fulbright Commission and the U.S.A.-Spain Joint Committee for postdoctoral support.

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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Received June 21, 1983

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.

0020-1669/84/1323-0343$01.50/0