dron. If a further choice is needed, the following should be applied in sequence:

a. The reference axis should have a terminal plane with the fewest number of polyhedral vertices.

b. The reference axis should lie in the reference plane (see principle 3, below).

2. Select the preferred terminal plane of symmetrically equivalent vertices, which defines the preferred end of the reference axis. The preferred terminal plane (a) contains the fewer number of polyhedral vertices, and if these are the same, (b) contains the vertices with the fewer total number of skeletal connectivities, i.e., the fewer number of polyhedral edges associated with the vertex.

If a further choice is needed, the preferred terminal plane is nearer to the parallel plane of symmetrically equivalent vertices preferred by applying criteria 2(a) and 2(b), above, successively to pairs of parallel planes proceeding inward from each terminal plane.

3. Select the reference plane, i.e., a symmetry plane or, if none, an arbitrarily defined plane containing the reference axis and at least one vertex not on the reference axis in a terminal plane or adjacent parallel plane. If there is more than one such plane containing the reference axis, or if selection of a reference axis was not effected by principle 1, above, the reference plane is chosen by applying the following criteria, sequentially, until a decision is made:

a. (i) If the polyhedron has at least one symmetry plane, the reference plane passes through the fewest number of polyhedral vertices. (ii) If the polyhedron does not have a symmetry plane, the reference plane has the fewest number of perpendicular planes defined by sets of polyhedral vertices that are either symmetrically equivalent or connectively equivalent, i.e., that have the same number of polyhedral edges associated with the vertex.

b. The reference plane passes through a polyhedral vertex that is nearer to the preferred terminal plane (see principle 2, above); i.e., polyhedral vertices in the reference plane have lower locant numbers when assigned according to principles 4-6, below.

c. The reference plane passes through a polyhedral vertex with the fewest number of associated polyhedral edges; i.e., polyhedral vertices with the lowest skeletal connectivity in the reference plane have the lower locant numbers when assigned according to principles 4-6, below.

4. Orient the polyhedron, in order to provide a consistent reference point for numbering, by looking down the reference axis from the preferred end (see principle 2, above) and rotating the polyhedron until the reference plane (see principle 3, above) is vertical. If a choice is needed, the preferred orientation has a polyhedral vertex of the preferred terminal plane, or in a parallel plane nearest to it, at the top of the orientation in the reference plane.

5. Determine the direction for numbering, if the reference plane of the polyhedron is *not* a symmetry plane, by noting the direction from the reference plane of the directional vertex, i.e., the vertex in the directional plane nearest to the top of the projection of the reference plane. The directional plane is the terminal plane at the end of the reference axis opposite to the preferred terminal plane, or if this terminal plane contains only one vertex, the directional plane is a parallel plane of polyhedral vertices adjacent to it.

6. Number the vertices of the polyhedron consecutively, clockwise or anticlockwise, starting with vertices in the preferred terminal plane and proceeding successively to succeeding planes of vertices working down the reference axis from the preferred end. The vertices in each plane are numbered in the same direction as the preceding and/or following planes, beginning in each plane with a vertex at the top of the preferred orientation (see principle 4, above), in the reference plane, or with the first vertex encountered, in the direction chosen, or required, for numbering, from the top of the preferred orientation. For chiral polyhedra in which the reference plane is arbitrarily defined, a vertex at the top of the preferred orientation need not be exactly in the reference plane but should be very close.

Notes

Contribution from the Department of Chemistry,
University of California, Santa Barbara, California 93106

Carbon-13 NMR Spectrum of $[Ir(bpy)_2H_2O(bpy)]Cl_3$: Further Indication of a Monodentate Bipyridine Structure

Peter J. Spellane and Richard J. Watts*

Received September 3, 1980

In this report we present NMR spectra of the hydrated tris(bipyridyl)iridium complex whose synthesis and UV-visible spectra were reported in 1977 and whose structure has been debated.[1-3] The most likely candidates for the structure are represented in Figure 1: (A) one which features a monodentate bipyridine and a water bound directly to the metal; (B) a "covalent hydrate" in which water is added across a carbon-nitrogen double bond. In view of the detailed structural information obtained from NMR spectra of transition-metal complexes of 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen),[4-8] we consider the structural implications of ^1H and

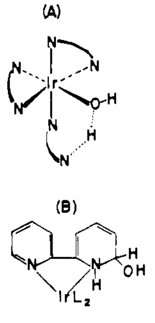


Figure 1. Possible solution structures of $[Ir(bpy)_2H_2O(bpy)]Cl_3$: (A) monodentate bipyridine with H_2O bound to the metal; (B) Covalent hydrate.

---

(1) Watts, R. J.; Harrington, J. S.; Van Houten, J. *J. Am. Chem. Soc.* **1977**, *99*, 2179.

(2) Gillard, R. D.; Lancashire, R. J.; Williams, P. A. *J. Chem. Soc., Dalton Trans.* **1979**, 190.

(3) Kahl, J. L.; Hanck, K.; DeArmond, K. *J. Inorg. Nucl. Chem.* **1979**, *41*, 495.

(4) Farver, O.; Mønsted, O.; Nord, G. *J. Am. Chem. Soc.* **1979**, *101*, 6118.

(5) DeSimone, R. E.; Drago, R. S. *Inorg. Chem.* **1969**, *8*, 2517.

(6) Flynn, C. M.; Demas, J. N. *J. Am. Chem. Soc.* **1974**, *96*, 1959; **1975**, *97*, 1988.

(7) Dixon, K. R. *Inorg. Chem.* **1977**, *16*, 2618.

0020-1669/81/1320-3561$01.25/0 © 1981 American Chemical Society

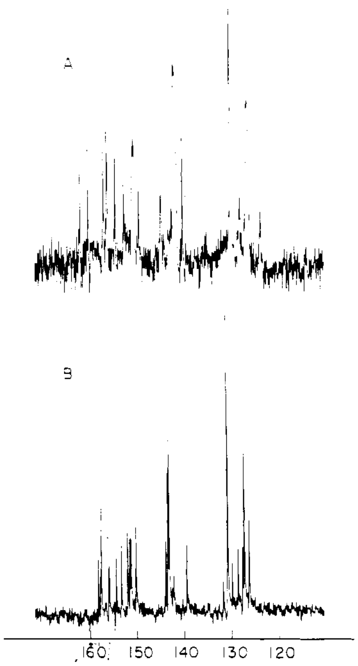


Figure 2. (A) Carbon-13 NMR of $[Ir(bpy)_2H_2O(bpy)]Cl_3$ in Me_2SO-d_6. This and all proton and carbon-13 NMR spectra were taken on a Varian CFT-20, which operates at 80 MHz in the proton mode and 20 MHz in the carbon mode. Spectra are Fourier transforms based on the number of accumulations which is specified for each spectrum. Chemical shifts are given in ppm downfield of Me_4Si. This spectrum was made from 78 036 accumulations. (B) Carbon-13 NMR of $[Ir(bpy)_2H_2O(bpy)]Cl_3$ in 0.1 N DCl (63 624 accumulations) signals were referenced to Me_4Si in the capillary.

Table I. Chemical Shifts (ppm) of Carbons of Several Bipyridyl Complexes[a]

	2	6	4	5	3	solvent	ref
pyr	150.0	150.0	136.2	124.0	124.0	$CDCl_3$	12
bpy	156.4	149.4	137.2	124.0	121.4	$CDCl_3$	12
IrB	156.9	151.2	144.1	130.7	127.4	H_2O/D_2O	6
Ir(aq)	157.4	151.4	143.3	130.6	127.3	DCl/D_2O	
Ir(aq)	156.2	150.4	141.7	129.9	126.3	Me_2SO-d_6	

[a] pyr = pyridine; bpy = bipyridine; IrB = $[Ir(bpy)_3](NO_3)_3$; Ir(aq) = $[Ir(bpy)_2H_2O(bpy)]Cl_3$ (the title complex). For Ir(aq), chemical shifts of the five broad lines are given; see text. Carbons are numbered at column tops according to standard bipyridine numbering scheme.

^{13}C NMR spectra of $[Ir(bpy)_2H_2O(bpy)]Cl_3$. The ^{13}C NMR spectrum in either Me_2SO-d_6 or DCl/D_2O shows resonances of aromatic carbons only, consistent with an inner sphere association of a water molecule with the complex. The proton NMR in Me_2SO-d_6 differs greatly from that in acidified D_2O; each spectrum is obtained from a sample recrystallized from the other solvent. The solvent dependence of the proton NMR suggests solvent dependence of the structure itself.

The ^{13}C NMR of the title complex (completely proton decoupled) consists of about 25 peaks in the region of 120–160 ppm downfield of Me_4Si (Figure 2). In this complex spectrum five broad resonances, each of which includes about four peaks, occur at chemical shifts nearly identical with those of $[Ir(bpy)_3](NO_3)_3$[6] (see Table I). When these broad resonances are substracted from the spectrum, 10 sharp lines remain. No resonance is evident in the spectrum obtained in either solvent in the region upfield of 120 ppm. ^{13}C resonances for covalently hydrated quinazolines, pteridines, and related molecules have been recently reported.[9–11] The covalently hydrated carbon of quinazoline (1,3-diazanaphthalene) resonates at 72.4 ppm downfield of Me_4Si,[9,10] and that of pteridine resonates at 73.9 ppm downfield of Me_4Si.[10,11]

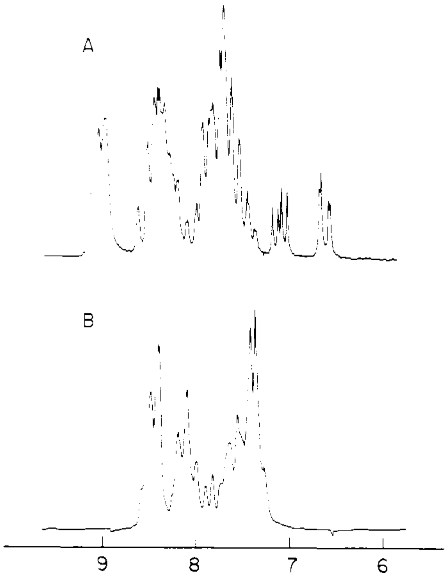


Figure 3. (A) Proton NMR of $[Ir(bpy)_2H_2O(bpy)]Cl_3$ in Me_2SO-d_6. This spectrum was made from 717 accumulations. (B) Proton NMR of $[Ir(bpy)_2H_2O(bpy)Cl_3$ in 0.1 N DCl. This spectrum was made from 1241 accumulations. Approximately 5% Me_2SO was added as a reference signal.

Proton NMR spectra of $[Ir(bpy)_2H_2O(bpy)]Cl_3$ in Me_2SO-d_6 and DCl/D_2O are shown in Figure 3. The Me_2SO-d_6 spectrum we obtain agrees well with published data,[2,3] including the presence of multiplets at 6.7 and 7.2 ppm downfield of Me_4Si, each of which integrates for 1 proton in 24. These high-field resonances which were cited as evidence for the covalent hydrate structure[2] are absent in acidified D_2O (Figure 3B) in which solvent hydration would be most probable. Solutions which have small amounts of DCl/D_2O added to Me_2SO-d_6 have proton NMR spectra intermediate between those measured in neat solvents.

As there is no evidence of an sp^3 carbon in the ^{13}C spectrum and as the high-field multiplets which could possibly arise from nonaromatic protons are absent in aqueous acid solution, we conclude that the water is not covalently bound to a bipyridine. All the data are consistent with the monodentate bipyridine structure we first proposed.[1] In this structure, all carbons retain their aromaticity. Furthermore, the four pyridine rings of the two bidentate bipyridines are nearly equivalent, accounting for the five broad ^{13}C resonances. The 10 carbon atoms of the monodentate bipyridine are responsible for the 10 sharp lines.

A solvent-dependent structure of the complex (twisting about the bridging carbon–carbon bond or fluctional behavior of the unique bipyridine similar to that reported for *cis*-$[PtCl(PEt_3)_2(phen)]^+$[7] and for the $[Pt(phen)_2(CN)]^+$[8]) could account for the extraordinary solvent dependence of the proton NMR. We are presently investigating the validity of these ideas.

Acknowledgment is made to the Division of Basic Energy Sciences of the Department of Energy, Contract DE-AS03-

---

(8) Wernberg, O.; Hazell, A. *J. Chem. Soc., Dalton Trans.* **1980**, 973.

(9) Ewers, U.; Gronenborn, A.; Günther, H.; Jaenicke, L. *Chem. Biol. Pteridines, Proc. Int. Symp., 5th* **1975**, 687.

(10) Ewers, U.; Günther, H.; Jaenicke, L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 354.

(11) Geerts, J. P.; Nagel, A.; van der Plas, H. C. *Org. Magn. Reson.* **1976**, *8*, 607.

(12) Marker, A.; Canty, A. J.; Brownlee, R. T. C. *Aust. J. Chem.* **1978**, *31*, 1255.

76SF00034, for support of this research. We wish to thank Matthey Bishop, Inc., Malvern, Pa., for the loan of the iridium used in this study. We thank Wayne Tikkanen for assistance and advice in use of the Varian CFT-20.

Registry No. [Ir(bpy)$_2$H$_2$O(bpy)]Cl$_3$, 62793-15-1.

Contribution from the Department of Chemistry,
North Texas State University, Denton, Texas 76203

Site of M-CO Bond Breaking and Fluxionality in (*o*-Phenanthroline)tetracarbonylmetal Systems[1,2]

Gerard R. Dobson* and Khalil J. Asali

Received December 19, 1980

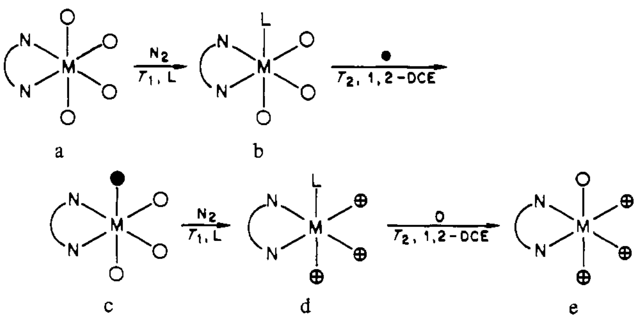
Since the controversy as to the site of Mn–C bond breaking in ligand-dissociation reactions of Mn(CO)$_5$Br (whether axial or equatorial[3])[4-9] and the discovery that five-coordinate intermediates derived through such a process may be fluxional on the time scale of the ligand-substitution process,[10] there has been a great interest in the elucidation of that site in substituted octahedral metal carbonyl systems and the determination of the extent of that fluxionality, if any. The systems Mn(CO)$_5$Br,[11,12] *cis*-Mn(CO)$_4$(PPh$_3$)(Br),[13] Re(CO)$_5$Br,[13] *cis*-Re(CO)$_4$(PPh$_3$)(Br),[13] (bpy)Cr(CO)$_4$,[14,15] (phen)Cr(CO)$_4$ (phen = *o*-phenanthroline),[14-16] and (diphos)Cr(CO)$_4$[17] [diphos = 1,2-bis(diphenylphosphino)ethane] have all been investigated in this context. Recently, also, it has been proposed that under kinetic control, product stereochemistry must reflect the site of initial M–CO bond breaking, regardless of possible fluxionality of the intermediate thus produced, in systems in which the incoming nucleophile creates little steric congestion during the substitution process.[18]

To ascertain whether the observed patterns of reactivity—stereospecific or highly stereoselective *axial* loss of CO and fluxional intermediates—hold for M = Mo and W as well as for Cr in the group 6B systems, the site of bond breaking and the extent of intermediate fluxionality have been determined for (phen)M(CO)$_4$ (M = Mo, W). Those results are the subject of this report.

Experimental Section

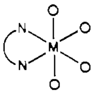
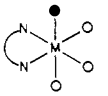
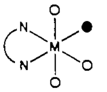
The method chosen for determination of the site of bond breaking—stereospecific introduction of a ^{13}CO label (90 mol %) and determination of its fate during the ligand-substitution process—is similar to that previously employed in the (phen)Cr(CO)$_4$ and (bpy)Cr(CO)$_4$ studies.[15] The substrates (phen)Mo(CO)$_4$ and (phen)W(CO)$_4$ and the *fac*-(CH$_3$CN)(phen)M(CO)$_3$ complexes which are employed in the sterospecific enrichment were prepared through standard procedures.[19,20] Scheme I sets forth the experimental conditions and the transformations employed in these studies.

Scheme I



M = Mo, T_1 = 50 °C, T_2 = 0 °C
M = W, T_1 = 82 °C, T_2 = 22 °C
N N = phen, ○ = ^{12}CO, ● = ^{13}CO, ⊕ = "scrambled" sites, L = CH$_3$CN

Table I. Site of Bond Breaking and Degree of Scrambling in (phen)M(CO)$_4$ Complexes (M = Mo, W)

	fraction present		
		exptl	
isotopic species	theory[a]	(phen)Mo(CO)$_4$ T_2 = 0 °C	(phen)W(CO)$_4$ T_2 = 22 °C
	0.5266	0.554	0.533
	0.1568	0.150	0.155
	0.3017	0.281	0.297

[a] For 100% scrambling and exclusive axial loss of CO. See ref 16.

The qualitative determination of the amount and position of the label in structures c and e (Scheme I) was made through use of a Perkin-Elmer Model 621 grating spectrophotometer and a JEOL FT-100 Fourier transform NMR spectrometer as described previously.[16] Results (experimentally determined percentages in the three predominant reaction products, nonlabled, and singly labeled either axial or equatorial), together with calculated results based on exclusive axial loss and subsequent statistically random label distribution, are presented in Table I.

Results and Discussion

In contrast to (phen)Cr(CO)$_4$,[21] which undergoes ligand exchange exclusively via a unimolecular, ligand-dissociation path, both (phen)Mo(CO)$_4$ and (phen)W(CO)$_4$ react by way of a two-term rate law (eq 1) indicative of two competitive

$$-d[(\text{phen})M(CO)_4]/dt = k_1[(\text{phen})M(CO)_4] + k_2[(\text{phen})M(CO)_4][L] \qquad (1)$$

reaction paths.[22] There is very strong evidence that these two paths, dissociation (D) and a dissociative interchange (I$_d$), are very closely related;[23,24] that both reaction paths afford the

---

(1) Octahedral Metal Carbonyls. 51.
(2) Taken from: Asali, K. J. Ph.D. Dissertation, North Texas State University, Denton, TX, 1979.
(3) Axial refers to an arrangment in which the carbonyl in question is trans to another carbonyl.
(4) Wojcicki, A.; Basolo, F. *J. Am. Chem. Soc.* **1961**, *83*, 525.
(5) Hieber, W.; Wollmann, K. *Chem. Ber.* **1962**, *95*, 1552.
(6) Kaesz, H. D.; Bau, R.; Hendrickson, D.; Smith, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2844.
(7) Johnson, B. F. G.; Lewis, J.; Miller, J. R.; Robinson, B. H.; Wojcicki, A. *J. Chem. Soc. A* **1967**, 522.
(8) Brown, T. L. *Inorg. Chem.* **1968**, *7*, 2673.
(9) Robinson, P. W.; Wojcicki, A. *Inorg. Chem.* **1971**, *10*, 2081.
(10) Darensbourg, D. J.; Darensbourg, M. Y.; Dennenberg, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 2807.
(11) Berry, A.; Brown, T. L. *Inorg. Chem.* **1972**, *11*, 1165.
(12) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3380.
(13) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3155.
(14) Dokiya, M.; Johnston, R. D.; Basolo, F. *Inorg. Chem.* **1970**, *9*, 996.
(15) Cohen, M. A. Brown, T. L. *Inorg. Chem.* **1976**, *15*, 1417.
(16) Dobson, G. R.; Asali, K. J. *J. Am. Chem. Soc.* **1979**, *101*, 5433.
(17) Dobson, G. R.; Asali, K. J.; Marshall, J. L.; McDaniel, C. R., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 8100.
(18) Dobson, G. R. *Inorg. Chem.* **1980**, *19*, 1413.
(19) Stiddard, M. H. B. *J. Chem. Soc.* **1962**, 4712.
(20) Houk, L. W.; Dobson, G. R. *Inorg. Chem.* **1966**, *5*, 2199.
(21) Angelici, R. J.; Graham, J. R. *Inorg. Chem.* **1967**, *6*, 988.
(22) Graham, J. R.; Angelici, R. J. *Inorg. Chem.* **1967**, *6*, 992.
(23) Covey, W. D.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2820.
(24) Pardue, J. E.; Dobson, G. R. *Inorg. Chim. Acta* **1976**, *20*, 207.