Table VII. Hydrogen Bonding in $Cu(C_8H_{11}N_2O_2)_2 \cdot 2H_2O^a$

atoms a–b···c	ac, Å	bc, Å	abc, deg
$O(3)^{vi}–H(13)^{vi}\cdots N(1)$	2.807	1.94	178
$O(3)–H(12)\cdots O(1)$	2.731	1.87	161
$O(2)^{iii}–H(10)^{iii}\cdots O(3)$	2.784	1.90	171
$N(2)–H(7)\cdots O(3)^{viii}$	3.085	2.37	145
$N(2)–H(6)\cdots N(1)^{vii}$	3.233	2.32	160

[a] See Figure 2 for symmetry superscripts.

layers are related to each other by the *a*-glide planes perpendicular to the *z* axis.

The water molecule O(3) is hydrogen bonded to two of the ligand atoms of a given copper atom. It acts as a donor to a phenolate oxygen atom O(1) and as an acceptor from the hydroxymethyl group $O(2)^{iii}$ (Figure 2). The main connection between the layers is provided by a hydrogen bond from the water molecule to a pyridine nitrogen atom in a neighboring layer. These three hydrogen bonds are of moderate strength, as indicated by the distances and the O–H···N and O–H···O angles (Table VII). Hydrogen bonding by the amino groups, which played such an important role in the structure of $Cu(PM)_2(NO_3)_2 \cdot H_2O$, appears not to occur in $Cu(PM\text{-}H)_2 \cdot 2H_2O$. The closest contacts involving the amino groups (Table VII) are essentially at van der Waals distances.

Acknowledgment. We thank the National Research Council of Canada for supporting this research. We are also grateful to Mrs. Terry Franklin for growing the crystals and to Mr. Walter Balenovich for drawing the packing diagram of $Cu(PM\text{-}H)_2 \cdot 2H_2O$.

Registry No. $Cu(PM)_2(NO_3)_2 \cdot H_2O$, 73505-56-3; $Cu(PM\text{-}H)_2 \cdot 2H_2O$, 73505-58-5.

Supplementary Material Available: Listings of structure factor amplitudes for $Cu(PM)_2(NO_3)_2 \cdot H_2O$ and $Cu(PM\text{-}H)_2 \cdot 2H_2O$ and Tables VIII and IX, distances and angles involving hydrogen atoms, and X and XI, least-squares planes (30 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Seven-Coordinate Carbonyl(5,7-dichloro-8-quinolinolato)(triphenylphosphine) Chelates of Tungsten(II)

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The structural complexities of seven-coordinate chelates with both hard and soft donors have been studied through a single-crystal X-ray diffraction study of tricarbonylchloro[5,7-dichloro-8-quinolinolato-*N*,*O*(1−)](triphenylphosphine)tungsten(II), $W(CO)_3Cl(dcq)(PPh_3)$, C_3, and dicarbonylbis[5,7-dichloro-8-quinolinolato-*N*,*O*(1−)](triphenylphosphine)tungsten(II), $W(CO)_2(dcq)_2(PPh_3)$, Q_2. Data for both complexes were collected on an Enraf Nonius CAD 4 diffractometer out to a maximum $2\theta_{Mo\,K\alpha}$ of 43°. C_3 crystallizes in the monoclinic space group $P2_1/n$, with $a = 14.623$ (5) Å, $b = 20.472$ (9) Å, $c = 9.916$ (4) Å, $\beta = 103.63$ (3)°, and $Z = 4$. Full-matrix least-squares refinement has led to $R = 0.042$ and $R_w = 0.055$ for the 2798 reflections having $I \geq 2\sigma_I$. Q_2 crystallizes as the CH_2Cl_2 1:1 solvate in the monoclinic space group, $P2_1/c$, with $a = 17.390$ (5) Å, $b = 15.300$ (6) Å, $c = 16.007$ (5) Å, $\beta = 115.50$ (2) Å, and $Z = 4$, and has been refined to the final values of $R = 0.054$ and $R_w = 0.067$ for the 3878 reflections having $I \geq \sigma_I$. We also include for comparison some preliminary structural results for the compound $W(CO)_2(PPh_3)_2(dcq)Cl$, P_2.

Introduction

In his recent extensive review, Drew[1] summarized structural information on 161 monomeric seven-coordinate complexes; however, none of the complexes present the wide array of donor atoms available in the three seven-coordinate W(II) complexes[2] synthesized recently in our laboratory. These chelates have carbonyl and phosphine π-acceptor ligands together with phenoxy anionic π donors and aromatic heterocyclic nitrogen donors as well as chloride π-donor ions in two of the three. Thus, these chelates posed an interesting test for the π-bonding structural relationships noted recently by Hoffmann et al.[3] As discussed below, the structures follow the predicted site preferences rather well even though the structures are appreciably distorted from any of the high-symmetry seven-coordinate polytopes.

We had previously proposed a possible generalized structure for the three chelates on the basis of these site preferences and similarities between the carbonyl stretching region of their infrared spectra and that of other molybdenum(II) and tungsten(II) seven-coordinate complexes with known structures[2] and can now examine the proposal.

These chelates are specifically dicarbonylbis[5,7-dichloro-8-quinolinolato-*N*,*O*(1−)](triphenylphosphine)tungsten(II), Q_2, tricarbonylchloro[5,7-dichloro-8-quinolinolato-*N*,*O*(1−)](triphenylphosphine)tungsten(II), C_3, and dicarbonyl[5,7-dichloro-8-quinolinolato-*N*,*O*(1−)]bis(triphenylphosphine)tungsten(II), P_2, where Q_2, C_3, and P_2 have been chosen to denote the unique ligands, e.g., the two quinolinol ligands in the first chelate.

The Q_2 and C_3 structures are well refined, whereas the data for P_2 are only of a preliminary quality.[4]

Experimental Section

Reagents. Reagent grade or equivalent solvents were used exclusively. These solvents were deoxygenated with nitrogen prior to use and subsequently used without further purification unless noted.

$W(CO)_3(PPh_3)(dcq)Cl$ (C_3) and $W(CO)_2(PPh_3)_2(dcq)Cl$ (P_2) were recrystallized from a crude reaction product[2] in which both were

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(1) Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67.
(2) Batschelet, W. H.; Archer, R. D.; Whitcomb, D. R. *Inorg. Chem.* **1979**, *18*, 48.
(3) Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *16*, 511.
(4) We included for comparison some preliminary results for the compound P_2 (space group $C2/c$ with $a = 23.997$ (10) Å, $b = 12.826$ (6) Å, $c = 29.926$ (9) Å, $\beta = 92.46$ (3)°, and $Z = 8$) on the basis of unit-weighted isotropic refinement using 3719 independent reflections having $I \geq 2\sigma_I$ and $2° \leq 2\theta_{Mo\,K\alpha} \leq 43°$ and giving $R = 0.135$. Because many of the isotropic thermal parameters seemed unreasonably small at this stage, we have abandoned further refinement until a better data set can be obtained.

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present. A 0.01-g sample of mixed product was dissolved in 1 mL of methylene chloride, and 3 mL of hexane was gradually added, leading to the formation of a dark precipitate. Then the mix was suction filtered, and two distinct types of crystals formed in the filtrate upon standing. The supernatant was decanted, and the solid was rinsed once with hexane and twice with ethanol. The crystals were covered with a small amount of ethanol and stored under a nitrogen atmosphere. At the end of 7 days, both orange crystals and a smaller amount of darker orange-brown crystals were present. The solvent was removed, and the crystals were dried in the dark in vacuo. On the basis of their infrared spectra, the orange crystals were identified as P_2 while the orange-brown crystals were C_3.

$W(CO)_2(PPh_3)(dcq)_2 \cdot CH_2Cl_2$ (Q_2) was obtained directly from a reaction mix prepared on a microscale by using approximately 2.5 times as much dry, deoxygenated solvent as previously published.[2] The reaction was run for 2 h at room temperature, sealed under a nitrogen atmosphere, and slowly cooled to 0 °C in the dark where it was maintained for 2 days. At the end of that time, the reaction mix was filtered, and the crystals were rinsed once with ethanol and dried under a nitrogen stream.

X-ray Diffraction Analysis of C_3. An irregularly shaped orange-brown transparent crystal, which can be described as roughly spherical with a diameter of 0.30 mm, was cut from a polycrystalline mass and sealed in a thin-walled glass capillary. Preliminary investigations using an Enraf-Nonius CAD 4 automated diffractometer and graphite-monochromated molybdenum radiation (fine-focus tube, 45 kV, 20 mA, takeoff angle = 3.1°, $\lambda(K\alpha_1) = 0.709\,30$ Å, $\lambda(K\alpha_2) = 0.713\,59$ Å) showed monoclinic ($2/m$) symmetry. From the observed extinctions $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, the space group was uniquely determined as $P2_1/n$ (alternate setting of $P2_1/c$–C_{2h}^5, No. 14[5]). The lattice constants as determined by the least-squares refinement of the diffraction geometry for 25 reflections having $11.52° \leq \theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 15.76°$ and measured at an ambient laboratory temperature of 23 ± 2 °C are $a = 14.623$ (5) Å, $b = 20.472$ (9) Å, $c = 9.916$ (4) Å, and $\beta = 103.63$ (3)°. A unit cell content of four molecules gives a calculated volume of 18.0 Å^3 per nonhydrogen atom, which falls in the range expected for such molecules. The assignment of $Z = 4$ was confirmed by successful solution and refinement of the structure.

Data were collected by using the θ–2θ scan mode with a θ scan range of $(0.65 \pm 0.35 \tan \theta)°$ centered about the calculated Mo $K\bar{\alpha}$ peak position. The scan range was actually extended an extra 25% on either side of the aforementioned limits for the measurement of background radiation. The scan rates varied from 0.7 to 4.0°/min, the rate to be used for each reflection having been determined by a prescan. The intensity, I, for each reflection is then given by $(\mathrm{FF}/S)(P - 2(\mathrm{B1} + \mathrm{B2}))$, where P are the counts accumulated during the peak scan, B1 and B2 are the left and right background counts, S is an integer which is inversely proportional to the scan rate, and FF is either unity or a multiplier to account for the occasional attenuation of the diffracted beam. The standard deviations in the intensities, σ_I, were computed as $\sigma_I^2 = (\mathrm{FF}/S^2)(P + 4(\mathrm{B1} + \mathrm{B2})) + 0.002I^2$. A total of 3289 independent reflections $(+h,+k,\pm l)$ having $2° \leq 2\theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 43°$ was measured. Six standard reflections, monitored after every 12 000 s of X-ray exposure time, gave no indication of crystal deterioration or loss of alignment. No corrections were made for absorption ($\mu_{\mathrm{Mo}\,K\bar{\alpha}} = 4.61$ mm^{-1}), and the intensities were reduced to relative amplitudes by means of standard Lorentz and polarization corrections, including corrections for the monochromator.

Initial coordinates for the tungsten atom were deduced from a Patterson synthesis, while initial coordinates for the remaining 39 independent nonhydrogen atoms were obtained by standard Fourier difference techniques. Isotropic unit-weighted full-matrix least-squares refinement[6] of the structural parameters for these 40 atoms and a scale factor gave a conventional residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.079 and a weighted residual $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ of 0.084 for the 2798 reflections having $I \geq 2\sigma_I$. Anisotropic refinement using variable weights ($w^{1/2} = 2F_oL_P/\sigma_I$) led to the final values of $R = 0.042$ and $R_w = 0.055$. During the last cycle of refinement, the largest shift in any parameter was 0.02 times its estimated standard deviation. The only peaks of any consequence on a final difference Fourier synthesis were in the immediate vicinity of the tungsten.

X-ray Diffraction Analysis of Q_2. Bright red transparent crystals of Q_2 become opaque and are easily crumbled within several days after removal from the mother liquor. Since this behavior is often a result of loss of solvent of crystallization, a near cubic specimen (0.25 × 0.30 × 0.32 mm) was cut from a freshly prepared larger crystal and was immediately sealed inside a thin-walled glass capillary. Experimental conditions for space group determination and data collection were the same as described for C_3, unless otherwise noted. Preliminary diffractometric investigations indicated monoclinic ($2/m$) symmetry. From the observed extinctions $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, the space group was uniquely determined as $P2_1/c$.[5] The lattice constants determined by using 25 reflections having $10.58° \leq \theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 14.94°$ are $a = 17.390$ (5) Å, $b = 15.300$ (6) Å, $c = 16.007$ (5) Å, and $\beta = 115.50$ (2)°. A unit cell content of four nonsolvated molecules gives a calculated volume of 19.2 Å^3 per nonhydrogen atom. It was therefore assumed that there were four molecules in the unit cell. The suspected presence of solvent of crystallization was confirmed by solution and refinement of the structure, leading to the formulation $W(CO)_2(PPh_3)(dcq)_2 \cdot CH_2Cl_2$, $Z = 4$.

A total of 4378 independent reflections was measured. The six standard reflections gave no indication of crystal deterioration or loss of alignment. No corrections were made for absorption ($\mu_{\mathrm{Mo}\,K\bar{\alpha}} = 3.69$ mm^{-1}).

Conditions for refinement were the same as described for C_3, unless otherwise noted. Initial coordinates for W were obtained from a Patterson synthesis. Initial coordinates for the remaining 49 atoms of the W complex were obtained in a series of difference Fourier syntheses, throughout which two disconnected strong peaks (~7 e/Å) about 3 Å apart persisted. Isotropic unit-weighted refinement of the structural parameters for the 50 atoms of the W complex and a scale factor gave $R = 0.119$ and $R_w = 0.146$ for the 3874 reflections having $I \geq \sigma_I$. A difference Fourier synthesis at this point showed the two aforementioned strong peaks with a smear of electron density nearby that suggested the presence of a CH_2Cl_2 molecule. The coordinates of the two strong peaks were assigned Cl scattering factors in subsequent unit-weighted refinement which led to $R = 0.090$ and $R_w = 0.097$. Since attempts to refine the solvent Cl atoms anisotropically seemed to slow convergence, they were included as isotropic contributions for the remainder of the refinement. Variable-weighted refinement (anisotropic for the W complex) led to $R = 0.065$ and $R_w = 0.083$. A difference Fourier synthesis at this point showed two peaks centered about a region where the C atom of the CH_2Cl_2 moiety might reasonably have been located. We interpreted these results as being due to static disorder, in which the two possible positions for CH_2Cl_2 were related by a swinging motion of the C atom between nearly pivotal positions for the Cl atoms, leaving for each Cl atom a pair of positions that were too close together to be resolved. Each of the two C positions were thus assigned C atom scattering factors with half-occupancy. Inclusion of these two half-atoms as isotropic contributions to the refinement led to the final values of $R = 0.054$ and $R_w = 0.067$ for the 3878 reflections having $I \geq \sigma_I$. During the last cycle of refinement, the largest Δ/σ was 0.06. The only peaks of any consequence on a final difference Fourier were in the vicinity of either the W atom or the Cl atoms of the solvent moiety.

Computations were done on a CDC CYBER-175 computer using LINEX, a modification of the Oak Ridge full-matrix least-squares program, ORFLS, Zalkin's Fourier program, FORDAP, Johnson's thermal ellipsoid plot program, ORTEP, the Oak Ridge FORTRAN function and error program, ORFFE, and several locally written programs.

Results

Figures 1–3 illustrate the molecular geometry and atom labeling for $W(CO)_3(PPh_3)(dcq)Cl$ (C_3), $W(CO)_2(PPh_3)(dcq)_2 \cdot CH_2Cl_2$ (Q_2), and $W(CO)_2(PPh_3)_2(dcq)Cl$ (P_2), respectively. Tables I–IV give the fractional atomic coordinates and the thermal parameters for C_3 and Q_2. The L–W–L angles for these structures are given in Table V together with those of the idealized seven-coordinate geometries: capped octahedron (CO), pentagonal bipyramid (PB), and capped trigonal prism (CTP). The average angular deviations for the three structures from the idealized geometries and between the idealized geometries are given at the bottom of this table.

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(5) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 99.

(6) The function minimized was $\sum w(|F_o| - |F_c|)^2$. Mean atomic scattering factors were taken from ref 5 (1974; Vol. IV, pp 72–89). Real and imaginary dispersion corrections for W, Cl, and P were taken from the same source, pp 149–150.

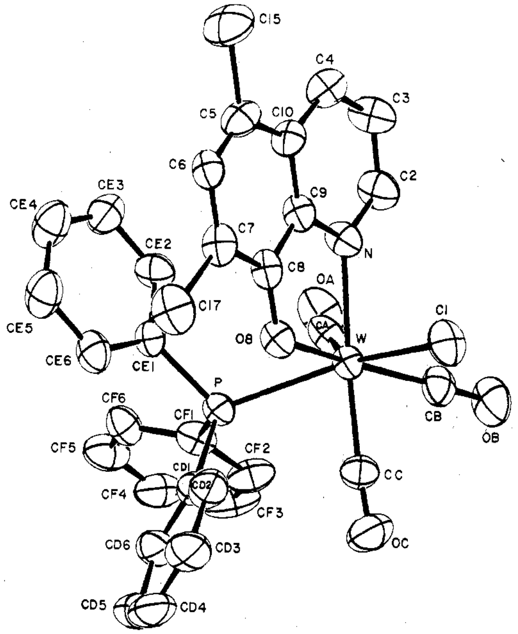


Figure 1. ORTEP plot of the $W(CO)_3(PPh_3)(dcq)Cl$, C_3, molecule. Thermal ellipsoids are shown at the 50% probability level.

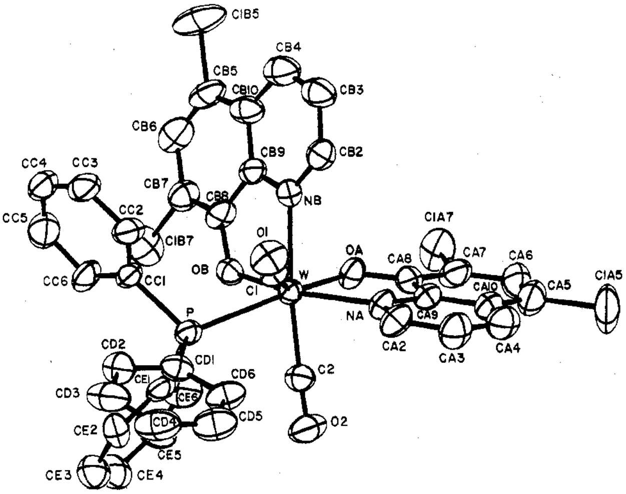


Figure 2. ORTEP plot of the $W(CO)_2(PPh_3)(dcq)_2$, Q_2, molecule. Thermal ellipsoids are shown at the 50% probability level.

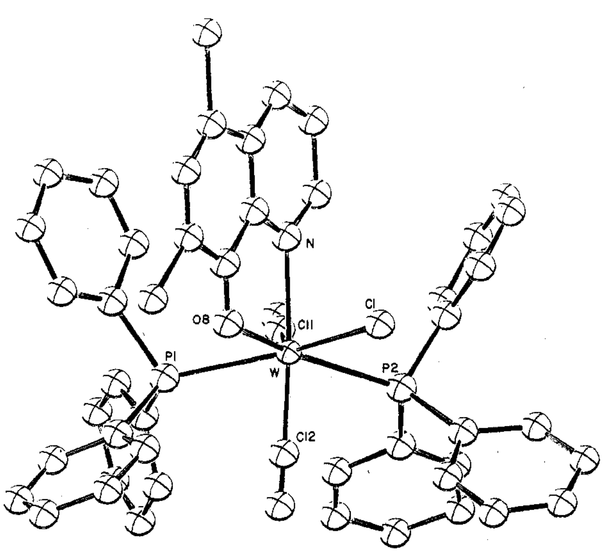


Figure 3. ORTEP plot of the $W(CO)_2(PPh_3)_2(dcq)Cl$, P_2 molecule. Atoms are represented by spheres of arbitrary radius.

Table I. Atomic Coordinates in Crystalline $W(CO)_3(PPh_3)(dcq)Cl$, C_3[a]

	coordinates		
atom type[b]	10^4x	10^4y	10^4z
W	2121.6 (3)	1745.3 (2)	1803.9 (4)
Cl	801 (2)	2504 (1)	1047 (3)
Cl7	3354 (2)	2796 (1)	−2100 (3)
Cl5	4585 (2)	4705 (1)	1610 (3)
P	3357 (2)	1006 (1)	1203 (2)
OA	3360 (5)	1303 (4)	4658 (7)
OB	772 (6)	1307 (4)	3688 (8)
OC	904 (5)	574 (4)	306 (8)
O8	2606 (4)	2203 (3)	185 (6)
N1	2817 (5)	2669 (4)	2740 (7)
CA	2929 (7)	1423 (5)	3590 (10)
CB	1276 (7)	1475 (5)	3008 (11)
CC	1361 (7)	993 (5)	801 (10)
C2	2895 (8)	2902 (5)	4022 (10)
C3	3335 (8)	3490 (5)	4478 (10)
C4	3732 (7)	3849 (5)	3606 (10)
C5	4029 (7)	3952 (5)	1198 (11)
C6	3917 (7)	3703 (5)	−93 (10)
C7	3447 (7)	3109 (5)	−444 (10)
C8	3045 (6)	2764 (4)	472 (9)
C9	3188 (6)	3040 (4)	1810 (9)
C10	3661 (6)	3624 (5)	2212 (10)
CD1	2963 (6)	630 (5)	−496 (9)
CD2	2484 (7)	1003 (5)	−1604 (11)
CD3	2160 (8)	710 (7)	−2961 (11)
CD4	2363 (9)	52 (7)	−3111 (12)
CD5	2821 (9)	−330 (6)	−2007 (11)
CD6	3160 (8)	−35 (5)	−694 (11)
CE1	4392 (6)	1482 (4)	1141 (9)
CE2	4862 (7)	1822 (4)	2317 (10)
CE3	5624 (7)	2227 (5)	2251 (11)
CE4	5925 (7)	2289 (6)	1041 (11)
CE5	5473 (8)	1933 (6)	−154 (11)
CE6	4696 (7)	1524 (5)	−126 (10)
CF1	3821 (7)	318 (4)	2317 (9)
CF2	3217 (7)	−48 (5)	2944 (10)
CF3	3570 (8)	−606 (5)	3730 (12)
CF4	4516 (7)	−785 (5)	3853 (11)
CF5	5106 (8)	−418 (5)	3283 (11)
CF6	4777 (7)	135 (5)	2503 (11)

[a] Numbers in parentheses are estimated standard deviations (esd's) in the last significant figure. [b] Atoms are labeled to agree with Figure 1.

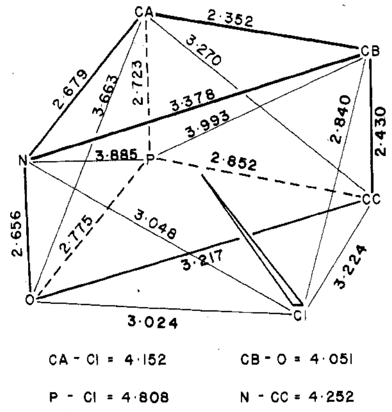


Figure 4. Distances (Å) between ligand atoms referred to the CTP coordination polyhedron for $W(CO)_3(PPh_3)(dcq)Cl$, C_3. Esd's are from 0.006 to 0.014 Å.

Table VI lists the bond lengths of the atoms coordinated to W for all three structures, while Tables VII and VIII contain the remaining bond lengths and angles for C_3 and Q_2, respectively. Interatomic distances between the atoms coordinated to W are given for C_3 in Figure 4 and for Q_2 in Figure 5.

Table II. Thermal Parameters in Crystalline $W(CO)_3(PPh_3)(dcq)Cl$, C_3[a]

atom type[b]	anisotropic parameters[c]					
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	0.0413 (3)	0.0329 (3)	0.0313 (3)	0.0040 (2)	0.0140 (2)	0.0066 (2)
Cl	0.059 (2)	0.052 (2)	0.058 (2)	0.021 (1)	0.018 (1)	0.015 (1)
Cl7	0.084 (2)	0.081 (2)	0.036 (1)	0.003 (2)	0.027 (1)	0.014 (1)
Cl5	0.087 (2)	0.061 (2)	0.084 (2)	−0.028 (2)	0.028 (2)	0.008 (2)
P	0.040 (1)	0.035 (1)	0.030 (1)	0.003 (1)	0.010 (1)	0.002 (1)
OA	0.086 (6)	0.071 (6)	0.037 (5)	0.025 (5)	0.015 (4)	0.013 (4)
OB	0.092 (6)	0.062 (5)	0.084 (6)	−0.003 (5)	0.063 (5)	0.014 (4)
OC	0.055 (5)	0.067 (5)	0.078 (6)	−0.015 (4)	0.005 (4)	−0.006 (5)
O8	0.054 (4)	0.039 (4)	0.029 (4)	0.004 (3)	0.018 (3)	0.009 (3)
N1	0.063 (6)	0.034 (5)	0.031 (5)	0.000 (4)	0.021 (4)	0.007 (4)
CA	0.070 (7)	0.036 (6)	0.036 (6)	0.010 (5)	0.023 (6)	0.006 (5)
CB	0.046 (6)	0.041 (6)	0.062 (7)	0.011 (5)	0.019 (6)	0.007 (5)
CC	0.046 (6)	0.050 (7)	0.037 (6)	−0.003 (6)	0.004 (5)	−0.006 (5)
C2	0.069 (7)	0.057 (8)	0.033 (6)	−0.002 (6)	0.015 (5)	0.001 (5)
C3	0.078 (8)	0.044 (6)	0.036 (6)	0.000 (6)	0.006 (6)	0.005 (5)
C4	0.046 (6)	0.050 (7)	0.046 (7)	−0.002 (5)	0.004 (5)	0.010 (5)
C5	0.044 (6)	0.043 (6)	0.060 (7)	−0.003 (5)	0.007 (5)	0.013 (6)
C6	0.048 (6)	0.038 (6)	0.049 (7)	0.007 (5)	0.024 (5)	0.011 (5)
C7	0.050 (6)	0.049 (7)	0.042 (6)	0.008 (5)	0.017 (5)	0.016 (5)
C8	0.041 (6)	0.037 (6)	0.033 (6)	0.010 (5)	0.016 (5)	0.016 (5)
C9	0.049 (6)	0.035 (6)	0.039 (6)	0.005 (5)	0.021 (5)	0.011 (5)
C10	0.043 (6)	0.035 (6)	0.048 (6)	0.001 (5)	0.015 (5)	0.014 (5)
CD1	0.036 (6)	0.055 (7)	0.031 (6)	−0.005 (5)	0.009 (5)	−0.008 (5)
CD2	0.051 (7)	0.076 (8)	0.044 (7)	−0.009 (6)	0.011 (6)	−0.009 (6)
CD3	0.076 (9)	0.091 (11)	0.041 (7)	−0.023 (7)	0.016 (6)	−0.019 (6)
CD4	0.078 (9)	0.086 (10)	0.061 (9)	−0.040 (8)	0.024 (7)	−0.030 (8)
CD5	0.083 (9)	0.060 (8)	0.056 (8)	−0.019 (7)	0.018 (7)	−0.015 (6)
CD6	0.063 (7)	0.060 (8)	0.049 (7)	−0.011 (6)	0.024 (6)	−0.015 (6)
CE1	0.035 (5)	0.040 (5)	0.036 (6)	0.007 (5)	0.011 (5)	0.004 (5)
CE2	0.056 (7)	0.050 (7)	0.028 (6)	−0.003 (5)	0.008 (5)	−0.004 (5)
CE3	0.044 (6)	0.061 (7)	0.064 (8)	−0.006 (6)	0.014 (6)	0.000 (6)
CE4	0.049 (7)	0.093 (9)	0.048 (7)	−0.007 (7)	0.015 (6)	0.005 (6)
CE5	0.054 (7)	0.092 (9)	0.047 (7)	−0.002 (7)	0.020 (6)	0.004 (6)
CE6	0.060 (7)	0.059 (7)	0.045 (6)	0.003 (6)	0.029 (6)	0.004 (5)
CF1	0.053 (6)	0.037 (6)	0.031 (5)	0.005 (5)	0.002 (5)	0.003 (4)
CF2	0.062 (7)	0.040 (6)	0.049 (6)	−0.013 (5)	0.001 (6)	0.013 (5)
CF3	0.075 (9)	0.039 (7)	0.069 (8)	−0.023 (6)	−0.013 (7)	0.011 (6)
CF4	0.057 (8)	0.040 (7)	0.064 (8)	0.000 (6)	−0.010 (6)	−0.001 (6)
CF5	0.063 (7)	0.040 (7)	0.066 (8)	0.009 (6)	−0.001 (6)	0.001 (6)
CF6	0.050 (7)	0.046 (7)	0.052 (7)	0.015 (5)	0.012 (5)	0.000 (5)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Atoms are labeled to agree with Figure 1. [c] Anisotropic thermal parameters are of the form $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.

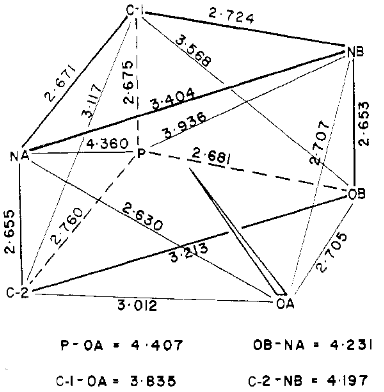
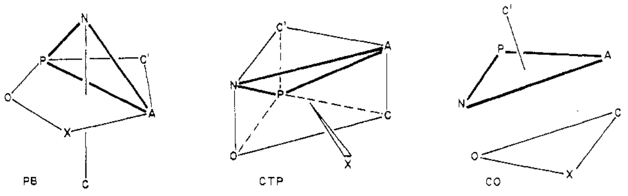


Figure 5. Distances (Å) between ligand atoms referred to the CTP coordination polyhedron for $W(CO)_2(PPh_3)(dcq)_2$, Q_2. Esd's are from 0.007 to 0.015 Å.

The coordination sphere about the central W atom for any of these structures cannot be described exactly in terms of any of the idealized seven-coordinate geometries (CO, PB, CTP). This can be seen by comparing the observed L–W–L angles (Table V) with those of the idealized polyhedra. Nor do the dihedral angles (Figure 6) give a clear indication that the structures are intermediate between any two of these. This is not surprising, since the idealized geometries have higher symmetries than the mixed ligand complexes reported here can be expected to realize. In addition, the effects of packing the bulky PPh_3 ligands and the planar 5,7-dichloro-8-quinolinolato (dcq^-) ligands in the crystalline solids, and the



	P	N	O	C	C'	A	X	C',N,A : N,A,X	C',N,P : N,P,O	C',P,A : P,A,C
Q2	P	NB	OB	C-2	C-1	NA	OA	44·8 (37·6)	24·1 (11·8)	-17·6 (-29·2)
C3	P	N	OB	CC	CA	CB	Cl	26·4 (29·3)	27·8 (16·4)	-8·0 (-15·2)
P2	P1	N	O8	C-12	C-11	P2	Cl	28·1 (21·7)	38·9 (26·9)	-13·3 (-27 7)
PB								54·4	54·4	-72·8
CTP								41·5	0	0
CO								24·2	24·2	24·2

Figure 6. Reaction pathways between PB, CTP, and CO geometries in terms of generalized atoms. The atom correspondence for the molecules Q_2, C_3, and P_2 is given on the lower left where the mirror image of Q_2 is used for purposes of comparison. The dihedral angles, δ, in degrees, including those for the idealized geometries, are given on the lower right and are indicated by the bold lines in the drawing. Values in parentheses are for the coordinated atoms transformed to a unit sphere. Negative dihedral angles are reentrant.

Table III. Atomic Coordinates in Crystalline $W(CO)_2(PPh_3)(dcq)_2 \cdot CH_2Cl_2$, Q_2[a]

	coordinates		
atom type[b]	10^4x	10^4y	10^4z
W	2343.6 (3)	4590.3 (3)	1654.4 (3)
ClA5	41 (3)	853 (3)	1848 (4)
ClA7	2976 (2)	1321 (2)	1566 (3)
ClB5	6669 (2)	3993 (3)	4798 (3)
ClB7	5050 (2)	4691 (2)	1163 (3)
P	2464 (2)	6065 (2)	1037 (2)
OA	2600 (4)	3246 (5)	1648 (5)
NA	1287 (5)	3906 (6)	1838 (6)
CA2	630 (7)	4257 (8)	1928 (8)
CA3	−26 (8)	3760 (9)	1981 (9)
CA4	−1 (7)	2857 (9)	1962 (9)
CA5	801 (8)	1561 (8)	1790 (9)
CA6	1489 (8)	1224 (8)	1714 (9)
CA7	2095 (7)	1786 (8)	1641 (8)
CA8	2057 (7)	2693 (7)	1704 (7)
CA9	1335 (6)	3023 (7)	1806 (7)
CA10	693 (7)	2473 (7)	1857 (8)
OB	3468 (4)	4648 (4)	1476 (5)
NB	3394 (6)	4363 (5)	3074 (6)
CB2	3331 (8)	4196 (8)	3858 (8)
CB3	4051 (9)	4006 (8)	4692 (8)
CB4	4852 (9)	3999 (8)	4710 (8)
CB5	5719 (7)	4201 (8)	3810 (9)
CB6	5757 (8)	4367 (8)	2992 (10)
CB7	4983 (7)	4521 (8)	2193 (8)
CB8	4208 (6)	4528 (7)	2222 (8)
CB9	4198 (7)	4348 (7)	3086 (7)
CB10	4951 (8)	4177 (8)	3897 (8)
C1	2034 (6)	5465 (7)	2348 (7)
O1	1890 (5)	5919 (6)	2849 (6)
C2	1426 (7)	4618 (7)	396 (7)
O2	866 (5)	4622 (6)	−338 (6)
CC1	3494 (6)	6596 (6)	1755 (7)
CC2	3642 (8)	6888 (8)	2640 (8)
CC3	4409 (8)	7292 (8)	3204 (9)
CC4	5045 (7)	7369 (8)	2915 (9)
CC5	4904 (8)	7058 (9)	2014 (10)
CC6	4118 (7)	6692 (8)	1429 (9)
CD1	1656 (7)	6909 (7)	911 (7)
CD2	1885 (8)	7788 (7)	947 (8)
CD3	1278 (10)	8427 (9)	808 (9)
CD4	441 (10)	8172 (9)	638 (9)
CD5	228 (8)	7295 (10)	601 (9)
CD6	830 (7)	6642 (8)	728 (8)
CE1	2453 (6)	6051 (7)	−115 (7)
CE2	2202 (8)	6812 (7)	−686 (8)
CE3	2225 (8)	6811 (9)	−1547 (9)
CE4	2505 (8)	6066 (10)	−1837 (9)
CE5	2752 (9)	5332 (8)	−1287 (8)
CE6	2708 (9)	5304 (8)	−423 (9)
Cl1	3365 (5)	1923 (5)	4208 (5)
Cl2	1818 (6)	2830 (6)	4246 (6)
CS1[c]	2848 (20)	2046 (21)	4704 (22)
CS2[c]	2074 (11)	2106 (12)	4238 (12)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Atoms are labeled to agree with Figure 2. Cl1, Cl2, CS1, and CS2 are solvate atoms. [c] Half-occupancy.

spacial requirements of these about W, might well be random deformations from idealized geometries. Both Q_2 and C_3 and the less well-refined P_2 show a similar van der Waals contact between the 7-chloro group of the dcq$^-$ and an aromatic phenyl ring of the PPh_3.

All of the W(II)–dcq$^-$ chelates have similar coordination sphere geometries. See Figure 6. C_3 and Q_2 appear to most closely approximate a CTP with an anionic (X) cap as noted from the angular data in Table V. For C_3 the atoms of the quadrilateral face (qf) of the CTP, CB, OB, N, and CC are coplanar to within ±0.1 Å (plane II, Table IX). The W atom is displaced 0.242 Å from this plane toward the e atoms, P and CA, which are in turn displaced from the plane by 2.273 and 1.851 Å, respectively. The capping atom, Cl, is on the opposite side of the qf at a distance of 2.194 Å. With the use of unit vectors (plane II*, Table IX), the coplanarity of the qf atoms is ±0.06 Å, W is 0.117 Å out of the plane, and the e atoms are displaced by 0.915 and 0.927 Å, while the cap is displaced by 0.875 Å, again in the opposite direction.

The analogous planes and deviations for Q_2 are given in Table X. Here, the coplanarity of the qf atoms NA, OB, NB, and C2 is not as good, being ±0.3 or ±0.1 Å for unit vectors, but otherwise the CTP is quite similar to that of C_3.

A CO structure with a carbonyl (C′) cap and both anions (X, O) in the uncapped face is only marginally poorer for C_3 and Q_2 and may actually be better for P_2 (see Table V). For C_3 in Table IX and for Q_2 in Table X, planes VII and VII* are defined by the atoms of the capped face (cf) of this CO, while planes VIII and VIII* are defined by the atoms of the uncapped face. The similarity of the distortions from ideal CO geometry for C_3 and Q_2 is easily visualized by comparing the displacements of the remaining atoms of the coordination sphere from the plane of the cf in each case. For ideal CO geometry, the dihedral angle between the planes of the cf and the uf would be 0°. For C_3, this angle is 16.7 or 13.4° with use of unit vectors, while for Q_2 the corresponding values are 16.6 and 16.0°.

The CTP and CO geometries are followed by a PB with carbonyl (C) and nitrogen (N) donors in the axial positions. Although the angles N–W–CC for C_3 (172.2 (3)°) and NB–W–C2 for Q_2 (172.3 (4)°) are not far from the value of 180° for the idealized PB, deviations from the least-squares mean plane through the girdle atoms in each case (plane I, Tables IX and X) show considerable departure from planarity. These deviations are, however, suggestive of a geometry intermediate between the PB and the CTP. In terms of the generalized atoms in Figure 6, to go from the PB to the CTP, A and O move away from X and N and C move toward X to form the qf of N, A, C, and O, while P and C′ twist out of the girdle plane to the e positions of the CTP. The twisting of the atoms P and C′ out of the girdle can be visualized in the deviations from the unit-vector least-squares mean planes I* of Tables IX and X. For C_3, P and CA are twisted out of the plane of CB, Cl, O8, and W; and less exactly for Q_2, P and C-1 are twisted out of the plane of NA, OA, OB and W. A second CTP with the other anionic donor (O) as the cap appears less favored than the aforementioned structures.

The structures can also be referred to a 4:3 geometry,[7] although, once again, the dihedral angles are not compelling. In terms of the generalized atoms in Figure 6, two of the qf atoms, A and C, along with the two e atoms C′ and P form the qf of the 4:3 geometry, while the three remaining atoms form the triangular face. For C_3, the 4:3 qf atoms are coplanar to within ±0.07 Å (plane III, Table IX), and the dihedral angle (δ_1) between this plane and the triangular face (plane V, Table IX) is 1.6°. The second dihedral angle δ_2 taken across the qf is either −8.0 or 6.7° depending on which face diagonal is used as the common edge. For unit vectors the angles become $\delta_1 = 1.1°$ and $\delta_2 = -15.2$ or 14.0°. The corresponding planes are given for Q_2 in Table X. In this case the 4:3 dihedral angles are $\delta_1 = 3.6°$ and $\delta_2 = -17.6$ or 12.6°, which become $\delta_1 = 4.2°$ and $\delta_2 = -29.2$ or 25.5° with use of unit vectors.

A pseudo-C_2 symmetry exists for P_2, which is also apparent in several other neutral tungsten(II) and molybdenum(II) seven-coordinate organometallic structures,[7-9] most of which

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(8) (a) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1977**, 557. (b) Drew, M. G. B.; Wilkins, J. D. *Ibid.* **1977**, 194.

(9) Mawby, A.; Pringle, G. E. *J. Inorg. Nucl. Chem.* **1972**, *34*, 517. One of the anionic donors is in the symmetry plane reported by these authors.

Table IV. Thermal Parameters in Crystalline $W(CO)_2(PPh_3)(dcq)_2 \cdot CH_2Cl_2$, Q_2[a]

	anisotropic parameters[c]					
atom type[b]	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	0.0267 (3)	0.0323 (3)	0.0361 (3)	−0.0014 (2)	0.0109 (2)	−0.0003 (2)
ClA5	0.086 (3)	0.066 (3)	0.148 (4)	−0.028 (2)	0.058 (3)	0.018 (3)
ClA7	0.061 (2)	0.046 (2)	0.112 (3)	0.009 (2)	0.038 (2)	−0.005 (2)
ClB5	0.049 (2)	0.099 (3)	0.083 (3)	0.033 (2)	−0.010 (2)	−0.022 (2)
ClB7	0.059 (2)	0.083 (3)	0.087 (3)	0.011 (2)	0.048 (2)	0.014 (2)
P	0.031 (2)	0.037 (2)	0.038 (2)	0.000 (1)	0.010 (1)	0.001 (1)
OA	0.032 (4)	0.041 (5)	0.061 (5)	−0.005 (4)	0.019 (4)	−0.004 (4)
NA	0.029 (5)	0.040 (6)	0.051 (6)	−0.003 (4)	0.016 (4)	−0.006 (5)
CA2	0.036 (7)	0.060 (8)	0.061 (8)	−0.004 (6)	0.021 (6)	−0.012 (6)
CA3	0.047 (8)	0.067 (9)	0.076 (9)	−0.002 (7)	0.032 (7)	0.000 (7)
CA4	0.045 (8)	0.078 (11)	0.061 (8)	−0.003 (7)	0.026 (7)	0.002 (7)
CA5	0.047 (8)	0.056 (9)	0.080 (10)	−0.011 (7)	0.023 (7)	0.003 (7)
CA6	0.064 (9)	0.042 (7)	0.073 (9)	−0.009 (7)	0.024 (7)	0.001 (7)
CA7	0.042 (7)	0.045 (8)	0.058 (8)	0.002 (6)	0.005 (6)	−0.002 (6)
CA8	0.046 (7)	0.032 (7)	0.044 (7)	−0.001 (6)	0.013 (6)	0.003 (5)
CA9	0.031 (6)	0.046 (8)	0.044 (7)	−0.002 (5)	0.012 (5)	0.001 (5)
CA10	0.033 (6)	0.052 (8)	0.053 (7)	−0.003 (6)	0.012 (6)	0.006 (6)
OB	0.039 (4)	0.037 (4)	0.043 (4)	0.003 (3)	0.016 (4)	0.007 (3)
NB	0.042 (6)	0.036 (6)	0.040 (6)	−0.004 (4)	0.018 (5)	0.003 (4)
CB2	0.063 (8)	0.041 (7)	0.047 (8)	−0.011 (6)	0.018 (7)	−0.006 (6)
CB3	0.072 (9)	0.045 (8)	0.050 (8)	0.007 (7)	0.016 (7)	0.005 (6)
CB4	0.071 (10)	0.045 (8)	0.054 (8)	0.006 (7)	0.007 (7)	−0.002 (6)
CB5	0.035 (7)	0.053 (8)	0.063 (9)	0.008 (6)	0.001 (7)	−0.007 (7)
CB6	0.046 (8)	0.050 (8)	0.081 (10)	0.005 (6)	0.019 (8)	−0.010 (7)
CB7	0.038 (7)	0.058 (8)	0.062 (8)	0.000 (6)	0.018 (6)	0.003 (6)
CB8	0.026 (6)	0.046 (7)	0.055 (7)	0.007 (5)	0.014 (6)	0.000 (6)
CB9	0.041 (7)	0.030 (6)	0.040 (7)	0.000 (5)	0.008 (5)	−0.002 (5)
CB10	0.055 (8)	0.042 (7)	0.046 (7)	0.011 (6)	0.011 (6)	0.000 (6)
C1	0.031 (6)	0.047 (7)	0.041 (6)	−0.002 (5)	0.011 (5)	0.003 (6)
O1	0.066 (6)	0.065 (6)	0.060 (5)	0.003 (5)	0.032 (5)	−0.014 (5)
C2	0.044 (7)	0.044 (7)	0.040 (7)	0.003 (6)	0.015 (6)	0.002 (6)
O2	0.052 (5)	0.078 (7)	0.053 (6)	−0.005 (5)	0.003 (5)	−0.005 (5)
CC1	0.032 (6)	0.032 (6)	0.044 (7)	−0.003 (5)	0.004 (5)	−0.002 (5)
CC2	0.054 (8)	0.049 (8)	0.047 (8)	−0.005 (6)	0.000 (6)	0.001 (6)
CC3	0.061 (9)	0.040 (8)	0.062 (8)	−0.006 (7)	−0.004 (7)	0.001 (6)
CC4	0.041 (8)	0.051 (8)	0.075 (10)	−0.008 (6)	0.000 (7)	0.010 (7)
CC5	0.058 (9)	0.058 (9)	0.088 (11)	−0.006 (7)	0.019 (8)	0.013 (8)
CC6	0.026 (6)	0.054 (8)	0.074 (9)	−0.006 (6)	0.010 (6)	0.003 (7)
CD1	0.043 (7)	0.053 (8)	0.041 (7)	0.010 (6)	0.017 (6)	0.005 (6)
CD2	0.071 (9)	0.029 (7)	0.054 (8)	0.005 (6)	0.021 (7)	−0.007 (6)
CD3	0.095 (11)	0.060 (9)	0.049 (8)	0.017 (8)	0.008 (8)	−0.001 (7)
CD4	0.080 (10)	0.065 (10)	0.064 (8)	0.027 (8)	0.007 (8)	−0.007 (8)
CD5	0.056 (9)	0.086 (11)	0.068 (9)	0.018 (8)	0.017 (7)	−0.005 (8)
CD6	0.032 (7)	0.074 (9)	0.060 (8)	0.015 (6)	0.013 (6)	−0.004 (7)
CE1	0.024 (6)	0.054 (8)	0.042 (6)	−0.004 (5)	0.006 (5)	−0.003 (6)
CE2	0.059 (8)	0.043 (7)	0.064 (8)	−0.004 (6)	0.034 (7)	0.010 (6)
CE3	0.056 (8)	0.073 (10)	0.061 (9)	−0.001 (7)	0.029 (7)	0.011 (7)
CE4	0.066 (9)	0.093 (12)	0.059 (9)	−0.001 (8)	0.036 (8)	0.019 (8)
CE5	0.082 (10)	0.063 (9)	0.047 (7)	0.018 (7)	0.036 (7)	0.002 (7)
CE6	0.077 (10)	0.058 (9)	0.060 (8)	0.014 (7)	0.028 (7)	0.011 (7)

	B_{iso}, Å^2		B_{iso}, Å^2		B_{iso}, Å^2		B_{iso}, Å^2
C11	13.5 (2)	C12	16.1 (2)	CS1[d]	6.7 (7)	CS2[d]	2.0 (3)

[a] See footnote *a*, Table II. [b] See footnote *b*, Table III. [c] See footnote *c*, Table II. [d] Half-occupancy.

have the metal and three neutral donors in the pseudo symmetry plane as is true for the complex being reported herein. Other low-symmetry approximations might also be envisioned from among the large numbers of topographical possibilities tabulated elsewhere. Alternatively, the structures might be viewed as being on the reaction coordinate between the CO described above and a second CO which has the neutral donor (A) in the capping position and both carbonyls and the anionic (X) donor in the capped face. This places the carbonyls in positions analogous to that observed in several other CO structures[11,12] and rationalizes the observed deviations from ideality for the L–M–L angles (Table V), especially the nearly linear arrangement of the N and C donors.

The bond distances (Table VI) appear to be typical for the donor atoms involved without any apparent lengthening for those atoms trans to carbonyls. In all three structures, one nitrogen donor bonds to the tungsten approximately trans to one of the carbonyls (≥172°, Table V) but without apparent lengthening of the tungsten–nitrogen bond.

Discussion

The structures of $W(CO)_3(PPh_3)(dcq)Cl$ (C_3), $W(CO)_2(PPh_3)(dcq)_2$ (Q_2), and $W(CO)_2(PPh_3)_2(dcq)Cl$ (P_2) are all very similar in spite of the fact that the species have either one or two bidentate ligands and one, two, or three large (P

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Table V. L-W-L Bond Angles (Deg) Grouped with Reference to the CTP[a]

C_3, Cl cap		Q_2, OA cap		P_2, Cl cap[c]		"ideal" CTP	"ideal" value for PB	"ideal" value for CO
				c-M-qf[b]				
Cl -W-O	82.4 (2)	OA-W-OB	80.2 (3)	Cl-W-O	78.0	82	72	89.6
-N	80.8 (2)	-NB	76.8 (3)	-N	75.8	82	90	76.6
-CB	78.7 (3)	-NA	74.4 (3)	-P2	75.6	82	72	76.6
-CC	91.7 (3)	-C2	95.6 (4)	-C12	102.7	82	90	89.6
				c-M-e				
Cl -W-CA	137.7 (3)	OA-W-C1	141.4 (4)	Cl -W-C11	131.7	144.2	144	125.5
-P	149.3 (1)	-P	145.4 (2)	-P1	149.2	144.2	144	160.4
				qf-M-qf (a)				
N-W-CB	105.8 (4)	NB-W-NA	98.7 (3)	N-W-P2	108.7	99	90	112.8
O-W-CC	102.0 (3)	OB-W-C2	104.7 (4)	O-W-C12	101.7	99	90	89.6
				qf-M-qf (b)				
N-W-O	75.0 (2)	NB-W-OB	75.2 (3)	N-W-O	70.8	78.7	90	76.6
CB-W-CC	74.6 (4)	NA-W-C2	78.1 (4)	P2-W-C12	77.8	78.7	90	76.6
				qf-M-qf (trans)				
N-W-CC	172.2 (3)	NB-W-C2	172.3 (4)	N-W-C12	172.5	164	180	160.4
O-W-CB	160.7 (3)	OB-W-NA	154.5 (3)	O-W-P2	152.7	164	144	160.4
				e-M-qf				
CA-W-CB	72.3 (4)	C1-W-NA	78.7 (4)	C11-W-P2	73.8	75.1	72	74.1
-N	78.2 (3)	-NB	80.5 (4)	-N	79.7	75.1	90	74.1
P-W-CC	76.7 (3)	P-W-C2	75.2 (3)	P1-W-C12	76.3	75.1	90	76.6
-O	72.6 (2)	-OB	70.6 (2)	-O	72.2	75.1	72	76.6
				e-M-qf				
CA-W-CC	109.1 (4)	C1-W-C2	105.5 (4)	C11-W-C12	106.2	118.9	90	125.5
-O	125.8 (3)	-OB	123.3 (3)	-O	130.8	118.9	144	125.5
P-W-N	108.8 (2)	P-W-NB	111.6 (2)	P1-W-N	101.1	118.9	90	112.8
-CB	123.6 (3)	-NA	133.2 (2)	-P2	132.4	118.9	144	112.8
				e-M-e				
CA-W-P	72.9 (3)	C1-W-P	72.4 (3)	C11-W-P1	76.1	71.5	72	74.1
av angular dev from								
CTP	4.7		5.4		7.9	0	12.3	6.1
PB	10.8		9.8		10.2		0	13.6
CO	5.5		7.7		7.5			0

[a] Atoms are labeled to agree with Figures 1-3. Esd's in parentheses. [b] We used the nomenclature and idealized angles of Drew (ref 1, p 78). [c] Esd's are 0.2-0.5°.

Table VI. Bond Lengths Involving W

C_3		Q_2		P_2	
type[a]	bond length, Å	type[a]	bond length, Å	type[a]	bond length, Å[b]
W-P	2.532 (2)	W-P	2.508 (3)	W-P1	2.490
W-N	2.242 (8)	W-NB	2.247 (9)	W-N	2.290
W-O8	2.120 (5)	W-OB	2.096 (7)	W-O8	2.126
W-CC	2.020 (10)	W-C2	1.959 (11)	W-C12	2.023
W-CA	1.995 (10)	W-C1	1.957 (11)	W-C11	1.967
W-CB	1.990 (10)	W-NA	2.241 (8)	W-P2	2.522
W-Cl	2.454 (3)	W-OA	2.106 (7)	W-Cl	2.480

[a] Atoms are labeled to agree with Figures 1-3. [b] Esd's are from 0.003 to 0.012 Å.

or Cl) donors. Therefore, these seven-coordinate structures appear to be largely electronically controlled within the limits allowed by the bidentate ligand bites and the donor atom repulsions.

The CTP which appears to best fit the distorted geometries of the complexes has several unique structural features relative to those discussed by Drew.[1] The only chelates which he considers to be CTP have one or two neutral, symmetrical bidentate ligands which span edges of the quadrilateral face. Since an oxygen donor of a chelating ligand provides the capped position in the Q_2 structure, only one of the bidentate ligands can occupy a quadrilateral edge for that chelate. And for C_3 the chelating ligand with oxygen as the CTP cap is only slightly less favorable than the CTP with Cl as the cap. These differences are not too surprising considering the unsymmetrical nature of the dcq$^-$ ligand with its anionic oxygen donor.

Predictions have been made for seven-coordinate structures with one[12] and two[13] bidentate ligands on the basis of bite considerations and electrostatic repulsions. For the C_3 complex with one bidentate ligand, the fact that our structure is similar to a CTP places it close to Kepert's stereochemistry D;[12] however, the observed deviations from CTP are not consistently in the directions predicted for that stereochemistry with one bidentate ligand of this bite. This may be due to the nonequivalence of the two ends of our bidentate ligand, the nonequivalence of the unidentate ligands, and the importance of nonequivalent metal–ligand interactions.

For the bis(bidentate) case, the predictions are not followed by the Q_2 species. This is not too surprising given the unsymmetrical nature of the chelating ligands and Kepert's consideration of only those situations where the two bidentates are related by a symmetry operation. The two bidentate ligands in Q_2 are not related by any such operation, and no direct comparison is possible.

Drew has discussed the influence of a chelate ring on distorting a CO into a CTP structure;[1] however, this is not believed to be the case with the dcq$^-$ chelates. Unlike the case

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(13) Kepert, D. L. *J. Chem. Soc., Dalton Trans.* **1975**, 963.

Table VII. Bond Lengths and Angles for the Ligand Groups for $W(CO)_3(PPh_3)(dcq)Cl$, C_3

type	bond length, Å	type	bond length, Å
P–CD1	1.819 (9)	CD1–CD2	1.384 (14)
P–CE1	1.813 (9)	CD2–CD3	1.446 (14)
P–CF1	1.820 (9)	CD3–CD4	1.394 (18)
CA–OA	1.125 (10)	CD4–CD5	1.383 (16)
CB–OB	1.162 (11)	CD5–CD6	1.415 (14)
CC–OC	1.126 (10)	CD6–CD1	1.415 (14)
C8–O8	1.315 (10)	CE1–CE2	1.393 (13)
C7–Cl7	1.738 (10)	CE2–CE3	1.402 (14)
C5–Cl5	1.746 (10)	CE3–CE4	1.378 (14)
N1–C2	1.338 (12)	CE4–CE5	1.416 (15)
C2–C3	1.390 (14)	CE5–CE6	1.417 (14)
C3–C4	1.364 (14)	CE6–CE1	1.430 (13)
C4–C10	1.438 (13)	CF1–CF2	1.410 (13)
C10–C5	1.417 (13)	CF2–CF3	1.410 (14)
C5–C6	1.351 (13)	CF3–CF4	1.408 (15)
C6–C7	1.401 (13)	CF4–CF5	1.363 (15)
C7–C8	1.385 (12)	CF5–CF6	1.392 (14)
C8–C9	1.411 (12)	CF6–CF1	1.417 (13)
C9–C10	1.392 (13)		

type	bond angle, deg	type	bond angle, deg
W–CA–OA	172.5 (9)	P–CF1–CF2	119.8 (7)
W–CB–OB	178.5 (9)	P–CF1–CF6	119.9 (7)
W–CC–OC	175.6 (9)	CF6–CF1–CF2	120.2 (9)
W–N–C2	128.5 (6)	CF1–CF2–CF3	119.3 (10)
W–N–C9	113.2 (6)	CF2–CF3–CF4	118.8 (10)
W–O8–C8	117.1 (5)	CF3–CF4–CF5	121.7 (10)
W–P–CD1	112.5 (3)	CF4–CF5–CF6	120.7 (10)
W–P–CE1	109.6 (3)	CF5–CF6–CF1	119.2 (10)
W–P–CF1	120.3 (3)	O8–C8–C9	120.6 (7)
CD1–P–CE1	106.3 (4)	O8–C8–C7	124.3 (8)
CD1–P–CF1	103.0 (4)	C7–C8–C9	114.9 (9)
CE1–P–CF1	104.0 (4)	Cl7–C7–C8	118.8 (8)
P–CD1–CD2	119.5 (8)	Cl7–C7–C6	118.6 (7)
P–CD1–CD6	120.4 (8)	C8–C7–C6	122.6 (9)
CD6–CD1–CD2	120.1 (9)	C7–C6–C5	120.4 (8)
CD1–CD2–CD3	120.2 (11)	C6–C5–C10	120.8 (9)
CD2–CD3–CD4	117.9 (12)	Cl5–C5–C6	120.0 (8)
CD3–CD4–CD5	122.5 (11)	Cl5–C5–C10	119.1 (8)
CD4–CD5–CD6	119.1 (11)	C5–C10–C9	116.8 (9)
CD5–CD6–CD1	119.9 (11)	C5–C10–C4	125.2 (9)
P–CE1–CE2	119.4 (7)	C4–C10–C9	118.0 (8)
P–CE1–CE6	119.8 (7)	C10–C4–C3	119.4 (9)
CE6–CE1–CE2	120.7 (9)	C4–C3–C2	119.6 (9)
CE1–CE2–CE3	119.8 (9)	C3–C2–N	123.2 (9)
CE2–CE3–CE4	121.1 (10)	C2–N–C9	118.2 (8)
CE3–CE4–CE5	119.9 (10)	N–C9–C10	121.4 (8)
CE4–CE5–CE6	120.4 (10)	N–C9–C8	114.1 (8)
CE5–CE6–CE1	118.0 (9)	C10–C9–C8	124.5 (8)

Table VIII. Bond Lengths and Angles for the Ligand Groups in $W(CO)_2(PPh_3)(dcq)_2$, Q_2

type	bond length, Å	type	bond length, Å
OA–CA8	1.298 (12)	ClB7–CB7	1.722 (12)
ClA7–CA7	1.740 (12)	ClB5–CB5	1.756 (11)
ClA5–CA5	1.741 (12)	C1–O1	1.166 (12)
NA–CA2	1.326 (13)	C2–O2	1.159 (12)
NA–CA9	1.356 (13)	P–CC1	1.848 (10)
CA2–CA3	1.404 (16)	P–CD1	1.854 (11)
CA3–CA4	1.384 (18)	P–CE1	1.835 (11)
CA4–CA10	1.416 (16)	CC1–CC2	1.399 (15)
CA10–CA9	1.428 (14)	CC2–CC3	1.394 (16)
CA10–CA5	1.417 (16)	CC3–CC4	1.375 (18)
CA5–CA6	1.356 (17)	CC4–CC5	1.437 (19)
CA6–CA7	1.403 (16)	CC5–CC6	1.399 (17)
CA7–CA8	1.396 (15)	CC6–CC1	1.401 (15)
CA8–CA9	1.427 (15)	CD1–CD2	1.396 (16)
OB–CB8	1.339 (12)	CD2–CD3	1.386 (17)
NB–CB2	1.331 (14)	CD3–CD4	1.415 (20)
NB–CB9	1.390 (14)	CD4–CD5	1.386 (19)
CB2–CB3	1.413 (16)	CD5–CD6	1.398 (17)
CB3–CB4	1.381 (18)	CD6–CD1	1.398 (16)
CB4–CB10	1.411 (17)	CE1–CE2	1.429 (15)
CB10–CB9	1.417 (15)	CE2–CE3	1.395 (16)
CB10–CB5	1.402 (17)	CE3–CE4	1.395 (18)
CB5–CB6	1.362 (18)	CE4–CE5	1.377 (18)
CB6–CB7	1.422 (17)	CE5–CE6	1.418 (17)
CB7–CB8	1.368 (15)	CE6–CE1	1.392 (16)
CB8–CB9	1.419 (15)		

type	bond angle, deg	type	bond angle, deg
W–C1–O1	172.0 (9)	CB9–CB10–CB4	116.6 (11)
W–C2–O2	177.8 (10)	CB10–CB4–CB3	120.1 (11)
W–OA–CA8	118.3 (6)	CB4–CB3–CB2	119.9 (11)
W–NA–CA2	128.2 (8)	CB3–CB2–NB	122.0 (11)
W–NA–CA9	113.2 (7)	CB2–NB–CB9	118.4 (9)
OA–CA8–CA9	118.7 (9)	NB–CB9–CB10	122.9 (10)
OA–CA8–CA7	125.7 (11)	NB–CB9–CB8	114.8 (9)
CA7–CA8–CA9	115.5 (10)	CB10–CB9–CB8	122.3 (10)
ClA7–CA7–CA8	118.8 (9)	CB9–CB8–CB7	117.2 (10)
ClA7–CA7–CA6	118.1 (9)	W–P–CC1	111.9 (3)
CA8–CA7–CA6	122.9 (12)	W–P–CD1	118.8 (4)
CA7–CA6–CA5	119.9 (12)	W–P–CE1	114.7 (4)
ClA5–CA5–CA6	119.2 (10)	CC1–P–CD1	104.3 (5)
ClA5–CA5–CA10	118.7 (10)	CC1–P–CE1	102.7 (5)
CA6–CA5–CA10	122.1 (11)	CD1–P–CE1	102.6 (5)
CA5–CA10–CA9	116.4 (11)	P–CC1–CC2	118.5 (8)
CA5–CA10–CA4	124.4 (11)	P–CC1–CC6	120.9 (8)
CA9–CA10–CA4	119.3 (11)	CC6–CC1–CC2	120.7 (10)
CA10–CA4–CA3	116.9 (11)	CC1–CC2–CC3	120.3 (12)
CA4–CA3–CA2	120.4 (11)	CC2–CC3–CC4	120.4 (12)
CA3–CA2–NA	123.2 (11)	CC3–CC4–CC5	119.6 (11)
CA2–NA–CA9	118.5 (9)	CC4–CC5–CC6	120.0 (13)
NA–CA9–CA10	121.6 (10)	CC5–CC6–CC1	118.9 (12)
NA–CA9–CA8	115.3 (9)	P–CD1–CD2	118.5 (9)
CA8–CA9–CA10	123.1 (10)	P–CD1–CD6	118.8 (9)
W–NB–CB2	125.8 (8)	CD6–CD1–CD2	122.6 (11)
W–NB–CB9	113.0 (6)	CD1–CD2–CD3	119.3 (12)
W–OB–CB8	117.9 (6)	CD2–CD3–CD4	119.0 (13)
OB–CB8–CB9	119.0 (9)	CD3–CD4–CD5	120.6 (13)
OB–CB8–CB7	123.7 (10)	CD4–CD5–CD6	121.3 (13)
ClB7–CB7–CB8	120.3 (9)	CD5–CD6–CD1	117.4 (12)
ClB7–CB7–CB6	117.3 (9)	P–CE1–CE2	120.1 (8)
CB8–CB7–CB6	122.4 (11)	P–CE1–CE6	119.9 (9)
CB7–CB6–CB5	118.4 (11)	CE6–CE1–CE2	119.9 (10)
ClB5–CB5–CB6	119.0 (10)	CE1–CE2–CE3	120.1 (11)
ClB5–CB5–CB10	118.1 (10)	CE2–CE3–CE4	119.5 (12)
CB6–CB5–CB10	122.9 (11)	CE3–CE4–CE5	120.8 (11)
CB5–CB10–CB9	116.7 (11)	CE4–CE5–CE6	121.0 (11)
CB5–CB10–CB4	126.7 (11)	CE5–CE6–CE1	118.7 (12)

of structures in which small bidentate bites led to distortions from a CO,[14] Table V indicates that the bite angle (N–W–O) is sufficiently close to the idealized value for a CO that it should be of only minor importance in causing distortions of possible CO structures.

The CTP (X cap) geometries shown in Figure 6 have all of the atoms in positions in agreement with the electronic arguments of Hoffmann et al.;[3] that is, an electronegative π donor is in the capping position and the other π donor is in the next most favorable position, the quadrilateral face. The π-acceptor ligands are in both the quadrilateral and edge positions, which are thought to be comparable sites for π acceptors. The CO (C′ cap) structural approximation has satisfactory placement for all but the one carbonyl (C) which is in the uncapped face, contrary to electronic predictions for π acceptors and structures of several other species.[1]

For the alternate structures, the CTP (O cap) has similar favorable atom placement to the CTP (X cap) discussed above. A CO (A cap) places the anionic π donor (X) in the uncapped face, a position which is electronically unfavorable[3] and which has not been observed.[1] The PB with axial carbonyl (C) and N donors has π acceptors in the preferred axial sites and π donors (X, O) in the more favorable equatorial sites and avoids the unfavorable arrangement of having the carbonyl groups

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(14) Drew, M. G. B.; Wolters, A. P.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1977**, 974.

Table IX. Deviations (Å) from Some Least-Squares Mean Planes for $W(CO)_3(PPh_3)(dcq)Cl$, C_3[a]

	I	II	III	IV	V	VI	VII	VIII
P	−0.591	(2.273)	−0.054	0.117			0.000	
CA	0.808	(1.851)	0.069	0.017			(1.381)	
CB	−0.395	−0.082	−0.060			0.000	0.000	
Cl	−0.058	(−2.194)			0.000	0.000	(−2.319)	0.000
O8	0.236	−0.121		−0.465	0.000		(−1.834)	0.000
N	(2.177)	0.111		0.330	0.000		0.000	
CC	(−2.022)	0.092	0.045			0.000	(−1.396)	0.000
W	(−0.012)	(0.242)	(−1.106)	(−1.126)	(1.526)	(1.393)	(−0.608)	

	I*[b]	II*	III*	IV*	V*	VI*	VII*	VIII*
P	−0.309	(0.915)	−0.063	0.044			0.000	
CA	0.470	(0.927)	0.074	−0.015			(0.725)	
CB	−0.069	−0.039	−0.045			0.000	0.000	0.000
Cl	−0.042	(−0.875)			0.000	0.000	(−0.992)	0.000
O8	−0.049	−0.062		−0.113	0.000		(−0.824)	0.000
N	(0.927)	0.058		0.084	0.000		0.000	
CC	(−0.991)	0.043	0.033			0.000	(−0.665)	0.000
W	(−0.019)	(0.117)	(−0.526)	(−0.516)	(0.674)	(0.649)	(−0.272)	

	N	C2	C3	C4	C5	C6	C7	C8	C9	C10	O8	Cl5	Cl7
IX	0.024	0.008	−0.020	0.001	0.008	−0.001	0.008	−0.028	−0.004	0.006	(−0.009)	(−0.053)	(0.050)
X	0.020	0.010	−0.007	0.016	0.018	0.001	0.000	−0.038	−0.006	0.014	−0.028	−0.031	0.033

Selected Dihedral Angles (Deg)

III-V = 1.6 IV-VI = 10.6 VII-VIII = 16.7 III*-V* = 1.1 IV*-VI* = 2.1 VII*-VIII* = 13.4

[a] Entries in parentheses are for atoms not included in the calculation of the plane. [b] Asterisks signify unit vectors.

Table X. Deviations (Å) from Some Least-Squares Mean Planes for $W(CO)_2(PPh_3)(dcq)_2$, Q_2[a]

	I	II	III	IV	V	VI	VII	VIII
P	−0.604	(1.996)	0.107	0.141			0.0	
C1	0.704	(2.061)	−0.070	−0.161			(1.408)	
NA	−0.385	−0.116	0.134			0.0	0.0	
OA	−0.019	(−1.738)			0.0	0.0	(−2.052)	0.0
OB	0.304	−0.218		−0.219	0.0		(−1.727)	0.0
NB	(2.15)	0.297		0.231	0.0		0.0	
C2	(−1.98)	0.036	−0.172			0.0	(−1.193)	0.0
W	(−0.034)	(0.293)	(1.060)	(1.131)	(1.482)	(1.315)	(−0.539)	

	I*	II*	III*	IV*	V*	VI*	VII*	VIII*
P	−0.308	(0.826)	0.089	0.041			0.0	
C1	0.324	(1.037)	−0.030	−0.040			(0.766)	
NA	−0.150	−0.054	0.119			0.0	0.0	
OA	0.021	(−0.827)			0.0	0.0	(−0.960)	0.0
OB	0.112	−0.095		−0.050	0.0		(−0.792)	0.0
NB	(0.948)	0.137		0.049	0.0		0.0	
C2	(−1.025)	0.012	−0.178			0.0	(−0.556)	0.0
W	(−0.032)	(0.139)	(0.498)	(−0.515)	(−0.692)	(0.636)		

	IX	X		XI	XII		IX(cont)	X(cont)		XI(cont)	XII(cont)
NA	−0.001	−0.003	NB	0.012	0.025	CA8	0.009	0.011	CB8	−0.004	0.024
CA2	−0.005	−0.000	CB2	0.008	0.008	CA9	0.013	0.011	CB9	−0.001	0.012
CA3	−0.013	−0.004	CB3	−0.011	−0.026	CA10	0.007	0.010	CB10	0.001	−0.001
CA4	0.015	0.026	CB4	−0.010	−0.026	ClA5	(−0.023)	−0.015	ClB5	(0.020)	0.002
CA5	−0.016	−0.014	CB5	0.016	0.015	ClA7	(0.049)	0.032	ClB7	(−0.087)	−0.041
CA6	0.011	0.007	CB6	0.008	0.021	OA	(−0.008)	−0.020	OB	(−0.062)	−0.021
CA7	−0.020	−0.029	CB7	−0.018	0.009						

Selected Dihedral Angles (Deg)

III-V = 3.6 IV-VI = 7.5 VII-VIII = 16.6 IX-XI = 79.5 X-XII = 80.2
III*-V* = 4.2 IV*-VI* = 6.5 VII*-VIII* = 16.0

[a] See footnotes to Table IX.

trans to each other. As mentioned above, significant deviations from planarity exist among the equatorial atoms.

The W–O and W–N bond length differences of about 0.14 Å for these structures are consistent with the values obtained for the tungsten(IV) chelate of 5-bromo-8-quinolinol.[14] As noted previously,[15] this difference is anticipated for d^n systems with only a few d electrons situated appropriately for π interactions. For d^0 chelates, the metal–oxygen distance is 0.24–0.38 Å greater than the metal–nitrogen distance and d^{8-9} chelates possess differences of less than 0.05 Å. The structure of Q_2 shows that the two bidentate ligands are nonequivalent in the solid state (Figure 2) while the room-temperature ^1H NMR exhibits only one sharp doublet (8.34 ppm downfield from Me_4Si, J = 8 Hz)[2] for the H(2) ring protons. Therefore, the single doublet is the result of either nonrigidity, which is well-known for seven-coordination,[16-18] or possibly a change

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(15) Bonds, W. D., Jr.; Archer, R. D.; Hamilton, W. C. *Inorg. Chem.* **1971**, *10*, 1764.

(16) Templeton, J. L., *Adv. Chem. Ser.* **1979**, *No. 173*, 263 and references therein.

Table XI. Comparison of C–M–C Angles, Carbonyl Stretching Frequencies, and Structures for Seven-Coordinate Tungsten(II) and Molybdenum(II) Tri- and Dicarbonyl Complexes

compd[a]	C–M–C angles, deg	CO str, cm^{-1}	structure	ref
$W(CO)_3(PPh_3)(dcq)Cl$	72, 75, 109	2017, 1939, 1904		
$W(CO)_3(dmpe)I_2$	72, 74, 104	2037, 1962, 1906	CO	11a, *b*
$W(CO)_3(difas)I_2$	71, 77, 108	2052, 1971, 1917	CO	11b, *c*
$W(CO)_3(dpam)I_2$	75, 76, 109	2042, 1970, 1922	CO	*d, e*
$Mo(CO)_3(dppe)Br_2$	73, 74, 108	2060, 1977, 1917	CO	11c, *f*
$Mo(CO)_3(r\text{-dimes})I_2$	74, 76, 105	2040, 1958, 1902	CO	12, *g*
$Mo(CO)_3(m\text{-dimes})I_2$	72, 75, 108	2045, 1980, 1925	CO	12, *g*
$Mo(CO)_3(PEt_3)_2Cl_2$	70, 75, 110	2004, 1946, 1886	CO	8b
$[W(CO)_3(PMe_2Ph)_3I]BPh_4$	100, 118, 118	2024, 1946, 1908	CO:CTP	*h, i*
$W(CO)_2(PPh_3)(dcq)_2$	106	1919, 1824		
$W(CO)_2(PPh_3)_2(dcq)Cl$	106	1920, 1826		
$W(CO)_2(t\text{-BuNC})_3I_2$	77	1978, 1915	4:3	7
$Mo(CO)_2(PMe_2Ph)_3Cl_2$	71	1934, 1842	CO:CTP	9, *i*
$Mo(CO)_2(PMe_2Ph)_3Br_2$	115	1934, 1834	CO	8a, *i*
$Mo(CO)_2(dpam)_2Cl_2$	71	1950, 1870	CO	14, *j*
$Mo(CO)_2(dpam)_2Br_2$	72	1950, 1870	CO:CTP	*k, j*
$Mo(CO)_2(dppm)Cl_2$	74	1940, 1865	CO:CTP	14, *l*
$[W(CO)_2(dmpe)_2I]I$	70 and 75	1951 and 1943, 1870 and 1851	CO:CTP and CTP	*m, b*
$[Mo(CO)_2(diars)_2Cl]I_3$	68	1960, 1888	CTP	*n, o*
av	72, 75, 108			*p*

[a] This study if not referenced; ligand abbreviations are as follows: diars, *o*-phenylenebis(dimethylarsine); difas, 2,3-bis(dimethylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene; dimas, *o*-phenylenebis(methylphenylarsine), *r* = racemic, *m* = meso forms; dmpe, bis(dimethylphosphino)ethane; dpam, bis(diphenylarsino)methane; dppe, bis(diphenylphosphine)ethane; dppm, bis(diphenylphosphino)methane; all structural assignments were taken from ref 1 unless otherwise noted. [b] Connor, J. A.; McEwen, G. K.; Rix, C. J. *J. Chem. Soc., Dalton Trans.* 1974, 589. [c] Cullen, W. R.; Mihichuk, L. *Can. J. Chem.* 1976, *54,* 2548. [d] Drew, M. G. B.; Wolters, A. P. *Acta Crystallogr., Sect. B* 1977, *33,* 205. [e] Colton, R.; Rix, C. J. *Aust J. Chem.* 1970, *23*, 441. [f] Anker, M. W.; Colton, R.; Rix, C. J.; Tomkins, I. B. *Ibid.* 1969, *22*, 1341. [g] Henrick, K.; Wild, S. B. *J. Chem. Soc., Dalton Trans.* 1974, 2500. [h] Drew, M. G. B.; Wilkins, J. D. *Ibid.* 1974, 1654. [i] Moss, J. R.; Shaw, B. L. *J. Chem. Soc. A* 1970, 595. [j] Anker, M. W.; Colton, R.; Tomkins, I. B. *Aust. J. Chem.* 1968, *21*, 1159. [k] Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* 1972, 626. [l] Anker, M. W.; Colton, R.; Tomkins, I. B. *Aust. J. Chem.* 1968, *21*, 1143. [m] Drew, M. G. B.; Wolters, A. P. *Acta Crystallogr., Sect. B* 1977, *33*, 1027. [n] Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* 1973, 2664. [o] Nigam, H. L.; Nyholm, R. S.; Stoddard, M. H. B. *J. Chem. Soc.* 1960, 1806. [p] Excluding $[W(CO)_3(PMe_2Ph)_3I]BPh_4$.

in stereochemistry upon dissolution. A temperature-dependent NMR study would be required to distinguish between these possibilities.

We had previously proposed a possible generalized structure relating Q_2, C_3, and P_2 on the basis of their infrared spectra, Hoffmann's site preferences,[3] and the structures of other tungsten(II) and molybdenum(II) di- and tricarbonyl seven-coordinate compounds.[2] As illustrated in Figure 6, the three compounds are closely related and can be interconverted by interchange of neutral and/or anionic donors. The structure originally proposed is in error, however, in the relationships between the carbonyl groups and in the symmetric nature assumed for the bis(bidentate) compound.

One interesting observation in comparing the structures reported here with those of other seven-coordinate tungsten(II) and molybdenum(II) di- and tricarbonyls is that, with the exception of $[W(CO)_3(PMe_2Ph)_3I]BPh_4$, all of the C–M–C angles can be placed into three very small ranges (Table XI). This is true whether the structure is described as CO, CTP, CO:CTP, or 4:3 and probably reflects the importance of electronic effects of the carbonyl groups in the determination of the overall geometry. Even from a tri- to a dicarbonyl complex, the remaining C–M–C angle falls into one of the three categories. The actual C–M–C angle observed may depend on a balance of forces, and in $[W(CO)_2(dmpe)_2I]I$ two distinct species are observed. Use of carbonyl stretching frequencies to generalize from one structure to another is potentially misleading as illustrated by comparison of $Mo(CO)_2(PMe_2Ph)_3Cl_2$ and $Mo(CO)_2(PMe_2Ph)_3Br_2$ which have very similar carbonyl stretches but widely different C–M–C angles. However, the infrared spectra were recorded as chloroform solutions, and which of the C–M–C configurations is adopted in the solid state may be a function of lattice forces. Thus electronic effects, especially of the carbonyl groups, appear to be of great importance in determining the overall geometry of these complexes. These in turn are probably influenced by other factors such as electrostatic repulsions, ligand bite, and lattice forces.

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Registry No. Q_2, 68036-87-3; C_3, 68036-89-5; P_2, 68036-88-4.

Supplementary Material Available: Observed and calculated structure factor amplitudes for C_3 and Q_2 (26 pages) Ordering information is given on any current masthead page.

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