Halocarbonyltungsten(II) Complexes Containing Tripodal Tris(pyrazolyl)borate Ligands

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The halo tricarbonyl complexes $LWX(CO)_3$ (X = I, Br, Cl) are formed when $NEt_4[LW(CO)_3]$ is reacted with I_2, *N*-bromosuccinimide, and *N*-chlorosuccinimide (or $PhICl_2$), respectively, while reaction of $NEt_4[L^{Pr}W(CO)_3]$ and I_2 yields $L^{Pr}WI(CO)_3$ [L = hydrotris(3,5-dimethylpyrazol-1-yl)borate, L^{Pr} = hydrotris(3-isopropylpyrazol-1-yl)-borate]. Reaction of $NEt_4[LW(CO)_3]$ with Br_2 yields mixtures of $LWBr(CO)_3$ and $L^{Br}WBr(CO)_3$ [L^{Br} = hydrotris-(4-bromo-3,5-dimethylpyrazol-1-yl)borate] as a result of competitive bromination of both tungsten and ligand L. The complexes generally exhibit three $\nu(CO)$ bands, one at ca. 2025 cm^{-1} and two between 1930 and 1900 cm^{-1}, and NMR spectra consistent with fluxional carbonyl-capped octahedral (C_s) structures. Crystals of $L^{Pr}WI(CO)_3 \cdot$MeOH are orthorhombic, space group *Pbca*, with a = 11.779(2) Å, b = 15.975(4) Å, c = 29.476(3) Å, and V = 5547(2) Å^3 for Z = 8. The seven-coordinate complex exhibits a 3:3:1 carbonyl-capped octahedral structure. In hot acetonitrile or tetrahydrofuran, the tricarbonyl complexes are converted into brown, paramagnetic (μ_{eff} ca. 1.15 μ_B) dicarbonyl species, $LWX(CO)_2$ and $L^{Br}WBr(CO)_2$, which exhibit two $\nu(CO)$ bands (ca. 1930 and 1840 cm^{-1}) and isotropically shifted NMR spectra consistent with a mononuclear structure with C_s symmetry. Further decarbonylation of $L^{Br}WBr(CO)_2$ in refluxing acetonitrile results in the formation of $L^{Br}WBr(MeCN-\kappa^2 N,C)$-(CO), which crystallizes in monoclinic space group *C2/c*, with a = 22.245(4) Å, b = 19.077(4) Å, c = 15.639(3) Å, β = 128.61(2)°, and V = 5286(2) Å^3 for Z = 8. The seven-coordinate complex features a "side-on" bonded, four-electron-donor acetonitrile ligand and a completely 4-brominated L^{Br} ligand.

Introduction

The first transition metal halo carbonyl complex, [PtCl$_2$-(CO)]$_2$, was described by Schutzenberger in 1868.[1] Since then, halo carbonyl complexes have been extensively studied and have underpinned many advances in organometallic chemistry.[2] In the late 1960s, important halo carbonyl complexes of Mo(II) and W(II), including the versatile starting materials M$_2$X$_4$(CO)$_8$ (M = Mo, W; X = Cl, Br, I), were prepared by Colton and co-workers;[3,4] these spawned a wealth of halocarbonyl−Mo and −W chemistry.[5] Around the same time, Trofimenko[6] reported the first organometallic poly(pyrazolyl)borate complexes, viz., [(HB(pz)$_3$)M(CO)$_3$]$^-$ and [LM(CO)$_3$]$^-$ [M = Cr, Mo, W; HB-(pz)$_3$ = hydrotris(pyrazolyl)borate; L = hydrotris(3,5-dimeth-ylpyrazol-1-yl)borate[7]]; this heralded the beginning of another extensive area of organometallic chemistry.[8] At the confluence of these two areas, the halo carbonyl poly(pyrazolyl)borate

complexes of chromium, molybdenum, and tungsten are yet to be fully described.

Curtis et al.[9,10] reported the synthesis and characterization of (HB(pz)$_3$)MoX(CO)$_3$ (X = Br, I); the crystal structure of (HB-(pz)$_3$)MoBr(CO)$_3$ revealed a seven-coordinate 4:3 piano stool structure, consistent with the observation of three $\nu(CO)$ bands by IR spectroscopy. The complexes are fluxional in solution on the NMR time scale, even at −80 °C; this is not unusual for seven-coordinate complexes, which can possess very low energy barriers to geometrical interconversions.[11] Templeton and co-workers extended this area with the generation in situ of LMoI-(CO)$_3$ and LMoI(CO)$_2$ and interpreted the solution infrared spectrum of the tricarbonyl, which features two $\nu(CO)$ bands, in terms of a C_{3v} structure.[12] Conflicting reports of the isolation and characterization of these complexes have recently appeared.[13,14] Subsequently, a number of halocarbonyltungsten complexes were prepared by the oxidation of $NEt_4[LW(CO)_3]$ by halogens.[15−18] The iodo carbonyl, LWI(CO)$_3$,[15] is well

(1) Schutzenberger, M. P. *Ann.* **1868**, *15*, 100.
(2) Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, U.K., 1982.
(3) (a) Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1966**, *19*, 1143. (b) Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1966**, *19*, 1519. (c) Anker, M. W.; Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1967**, *20*, 9. (d) Bowden, J. A.; Colton, R. *Aust. J. Chem.* **1968**, *21*, 2657. (e) Colton, R.; Rix, C. J. *Aust. J. Chem.* **1969**, *22*, 305.
(4) Dinuclear structures closely related to that postulated by Colton and Rix[3e] have been confirmed for the following: W$_2$Br$_4$(CO)$_8$ (see: Cotton, F. A.; Falvello, L. R.; Meadows, J. H. *Inorg. Chem.* **1985**, *24*, 514); Mo$_2$I$_4$(CO)$_8$ (see: Calderazzo, F.; Poli, R.; Zanazzi, P. F. *Gazz. Chim. Ital.* **1988**, *118*, 583).
(5) Baker, P. K. *Adv. Organomet. Chem.* **1996**, *40*, 45.
(6) Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 588.
(7) Abbreviations used: CO$_h$-CO$_{ax}$ = carbonyl-capped octahedron(ral); CO$_h$-X$_{ax}$ = halide-capped octahedron(ral); CTP = capped trigonal prism(atic) (when axial ligand specified: CTP-X$_{ax}$); HB(pz)$_3$$^-$ = hydrotris(pyrazolyl)borate; L = hydrotris(3,5-dimethylpyrazol-1-yl)-borate; L^{Br} = hydrotris(4-bromo-3,5-dimethylpyrazol-1-yl)borate; L^{Pr} = hydrotris(3-isopropylpyrazol-1-yl)borate.

(8) (a) Trofimenko, S. *Chem. Rev. (Washington, D.C.)* **1972**, *72*, 497. (b) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115. (c) Trofimenko, S. *Chem. Rev. (Washington, D.C.)* **1993**, *93*, 943.
(9) Curtis, M. D.; Shiu, K.-B.; Butler, W. M. *Organometallics* **1983**, *2*, 1475.
(10) Curtis, M. D.; Shiu, K.-B. *Inorg. Chem.* **1985**, *24*, 1213.
(11) (a) Kepert, D. L. *Prog. Inorg. Chem.* **1979**, *25*, 41. (b) Kepert, D. L. *Inorganic Stereochemistry*; Springer-Verlag: Berlin, 1982.
(12) Gamble, A. S.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 693.
(13) Cano, M.; Campo, J. A.; Heras, J. V.; Pinilla, E.; Monge, A. *Polyhedron* **1996**, *15*, 1705.
(14) Saleh, A. A.; Pleune, B.; Fettinger, J. C.; Poli, R. *Polyhedron* **1997**, *16*, 1391.
(15) Feng, S. G.; Philipp, C. C.; Gamble, A. S.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 3504.
(16) Feng, S. G.; Luan, L.; White, P.; Brookhart, M. S.; Templeton, J. L.; Young, C. G. *Inorg. Chem.* **1991**, *30*, 2582.

characterized and readily accessible and has served as a valuable precursor for a wide range of complexes.[19] The compound is fluxional at room temperature, but at low temperature it exhibits a static structure with C_s symmetry.[15] Brief reports of LWBr-$(CO)_3$,[16] LWI$(CO)_2$,[17] and LWBr$(CO)_2$[18] have appeared in connection with syntheses of carbonyloxo, thiolato, and μ-thio complexes, respectively. To date, no tungsten poly(pyrazolyl)-borate halo carbonyl has been structurally characterized. Some closely related halo carbonyl triazolylborate complexes of molybdenum have been reported by Shiu et al.[20] and Macleod et al.[21]

We were interested in the halo carbonyl poly(pyrazolyl)borate complexes of tungsten for several reasons. First, complexes of this type appeared to be promising precursors for novel carbonyloxo- and carbonylthiotungsten complexes.[22-24] Second, we wished to fully define the accessibility, stability, structure, and reactivity of this class of compound. Third, we were interested in extending known chemistry and in exploring the synthesis and properties of halocarbonyl−W(III) or −W(IV) complexes. Here, we present a detailed, systematic study of the halocarbonyl−W(II) complexes, LWX$(CO)_3$ and LWX$(CO)_2$ (X = Cl, Br, I); we report convenient syntheses, physical and spectroscopic data, and the X-ray crystal structure of the closely related complex, $L^{Pr}WI(CO)_3$ [L^{Pr} = hydrotris(3-isopropylpyra-zol-1-yl)borate[7]]. The 3:3:1 carbonyl-capped octahedral structure of $L^{Pr}WI(CO)_3$ is compared and contrasted with the structure of $(HB(pz)_3)MoBr(CO)_3$. Further, we describe the synthesis and characterization of NEt$_4$[$L^{Br}W(CO)_3$], $L^{Br}WBr$-$(CO)_3$, $L^{Br}WBr(CO)_2$, and $L^{Br}WBr(MeCN)(CO)$ [L^{Br} = hydro-tris(4-bromo-3,5-dimethylpyrazol-1-yl)borate], investigated in order to clarify the observed ligand 4-bromination of NEt$_4$[LW-$(CO)_3$] by Br$_2$; this work includes the X-ray crystal structure of $L^{Br}WBr(MeCN)(CO)$.

Experimental Section

Materials and Methods. Except for the syntheses of KL^{Br}, NEt$_4$[$L^{Br}W(CO)_3$], LWI$(CO)_3$, and $L^{Pr}WI(CO)_3$, all reactions were performed under an atmosphere of dinitrogen using dried, deoxygenated solvents and standard Schlenk techniques. With the exception of LWI-$(CO)_3$, the halo carbonyl complexes were routinely stored under an atmosphere of dinitrogen. Samples of 4-bromo-3,5-dimethylpyrazole,[25] KL^{Pr},[26] NEt$_4$[LW(CO)$_3$],[6] W(CO)$_3$(MeCN)$_3$,[27] and PhICl$_2$[28] were pre-

(17) Philipp, C. C.; Young, C. G.; White, P. S.; Templeton, J. L. *Inorg. Chem.* **1993**, *32*, 5437.

(18) Thomas, S.; Tiekink, E. R. T.; Young, C. G. *Inorg. Chem.* **1994**, *33*, 1416.

(19) (a) Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 8190. (b) Pérez, P.-J.; Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 7928. (c) Pérez, P.-J.; White, P. S.; Brookhart, M.; Templeton, J. L. *Inorg. Chem.* **1994**, *33*, 6050. (d) Powell, K. R.; Pérez, P.-J.; Luan, L.; Feng, S. G.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **1994**, *13*, 1851.

(20) Shiu, K.-B.; Lee, J. Y.; Wang, Y.; Cheng, M.-C.; Wang, S.-L.; Liao, F.-L. *J. Organomet. Chem.* **1993**, *453*, 211.

(21) Macleod, I. T.; Tiekink, E. R. T.; Young, C. G. *J. Organomet. Chem.* **1996**, *506*, 301.

(22) (a) Thomas, S.; Tiekink, E. R. T.; Young, C. G. *Organometallics* **1996**, *15*, 2428. (b) Thomas, S.; Young, C. G.; Tiekink, E. R. T. *Organometallics* **1998**, *17*, 182.

(23) Eagle, A. A.; Thomas, S.; Young, C. G. In *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*; Stiefel, E. I., Matumoto, K., Eds.; ACS Symposium Series, No. 653; American Chemical Society: Washington, DC, 1996; p 324.

(24) Thomas, S. Ph.D. Dissertation, University of Melbourne, 1997.

(25) Ohsawa, A.; Kaihoh, K.; Itoh, T.; Okada, M.; Kawabata, C.; Yamaguchi, K.; Igeta, H. *Chem. Pharm. Bull.* **1988**, *36*, 3838.

(26) Trofimenko, S.; Calabrese, J. C.; Domaille, P. J.; Thompson, J. S. *Inorg. Chem.* **1989**, *28*, 1091.

(27) Kubas, G. J. *Inorg. Chem.* **1983**, *22*, 692.

pared by literature methods. All other reagents were analytical reagent grade or above. Solid-state (KBr disk) and solution infrared spectra were recorded on a Jasco A-302 spectrophotometer. Proton NMR spectra were obtained using JEOL GX-400 and Varian 300 MHz FT NMR spectrometers and were referenced against internal solvent (CHCl$_3$, δ 7.26; CHD$_2$CN, δ 1.93; CHDCl$_2$ δ 5.32). Electronic spectra were recorded with a Perkin-Elmer 1430 spectrophotometer. The molar mass of LWI(CO)$_2$ was determined using vapor pressure osmometry by the Microanalytical Service at the Australian National University. Microanalyses were performed by Atlantic Microlabs, Norcross, GA.

Syntheses. LWCl(CO)$_3$. Method 1. *N*-Chlorosuccinimide (<0.85 g, 6.33 mmol) was added portionwise to a suspension of NEt$_4$[LW-(CO)$_3$] (4.0 g, 5.75 mmol) in dichloromethane (30 mL) until a clear red solution was formed, and then the mixture was stirred for 30 min. The volume of the red solution was reduced to ca. 10 mL, and then methanol (40 mL) was added to precipitate orange crystals. These were filtered out, washed with methanol, and dried in vacuo. Yield: 2.95 g, 85%. The compound can be recrystallized from dichloromethane/ methanol or dichloromethane/*n*-hexane.

Anal. Calcd for C$_{18}$H$_{22}$BClN$_6$O$_3$W: C, 36.00; H, 3.69; N, 14.00; Cl, 5.90. Found: C, 36.08; H, 3.75; N, 14.06; Cl, 5.96. ^{13}C{^{1}H} NMR (CDCl$_3$): At 30 °C, δ 12.44, 15.63 (CH$_3$); 107.57 (4-C); 144.55, 152.09 (CCH$_3$); 235.30 (CO). At −60 °C, δ 12.71, 13.39, 15.69, 15.92 (CH$_3$); 107.43, 107.95 (4-C); 144.66, 147.73, 151.40, 151.81 (CCH$_3$); 230.60 br, 246.90 br (CO).

Method 2. A suspension of NEt$_4$[LW(CO)$_3$] (4.0 g, 5.75 mmol) in dichloromethane (30 mL) was cooled to −78 °C. The cooling bath was removed, and as the stirred suspension warmed, a solution of PhICl$_2$ (1.70 g, 6.32 mmol) in dichloromethane (30 mL) was added dropwise over a period of 10 min. The mixture was allowed to stir for 1 h and then reduced to dryness in vacuo. The residue was treated with acetonitrile (60 mL), stirred to dissolve the bulk of the material, and then filtered to remove a small amount of LW(CO)$_3$. The filtrate was reduced in volume and diluted with methanol to precipitate the orange crystalline product, which was isolated by filtration, washed with methanol, and dried in vacuo. Yield: 2.10 g, 62%. Properties were identical to those of the sample prepared as above.

LWBr(CO)$_3$. *N*-Bromosuccinimide (1.14 g, 6.40 mmol) was added to a suspension of NEt$_4$[LW(CO)$_3$] (4.0 g, 5.75 mmol) in dichloromethane (30 mL), and the mixture was stirred for 60 min. The volume of the resultant red solution was reduced to ca. 10 mL, and then methanol (40 mL) was added to precipitate orange crystals. These were filtered out, washed with methanol, and dried in vacuo. Yield: 3.01 g, 81%. The compound can be recrystallized from dichloromethane/methanol or dichloromethane/*n*-hexane.

Anal. Calcd for C$_{18}$H$_{22}$BBrN$_6$O$_3$W: C, 33.52; H, 3.49; N, 13.03. Found: C, 33.44; H, 3.46; N, 13.11. ^{13}C{^{1}H} NMR (CDCl$_3$): At 30 °C, δ 12.63, 16.66 (CH$_3$); 107.80 (4-C); 144.85, 152.69 (CCH$_3$); 233.30 (CO). At −60 °C, δ 12.77, 13.38, 15.83, 16.60 (CH$_3$); 107.50, 107.90 (4-C); 144.87, 147.54, 151.29, 152.27 (CCH$_3$); 228.82 br, 245.19 br (CO).

KL^{Br}. A mixture of 4-bromo-3,5-dimethylpyrazole (25 g, 0.14 mol) and KBH$_4$ (2.55 g, 47 mmol) was heated at 210 °C for 2 h or until hydrogen gas evolution had ceased. The mixture was allowed to cool, and the white solid was extracted with dichloromethane (300 mL). The mixture was filtered, and the filtrate was treated with *n*-hexane (200 mL). The volume of the mixture was then reduced under vacuum to ca. 150 mL, and the white precipitate was isolated by filtration and washed with *n*-hexane. Yield: 18.85 g, 70%. The analytical sample was recrystallized from wet tetrahydrofuran/*n*-hexane as the monohy-drate.

Anal. Calcd for C$_{15}$H$_{21}$BBr$_3$KN$_6$O: C, 30.49; H, 3.58; N, 14.22. Found: C, 30.65; H, 3.49; N, 14.12. Mp: 315 °C (dec). IR (KBr): ν(BH) 2466, ν(CN) 1534 cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 2.04 (s, 9H, 3 × CH$_3$), 2.12 (s, 9H, 3 × CH$_3$).

NEt$_4$[L^{Br}W(CO)$_3$]. A suspension of W(CO)$_6$ (6.14 g, 17.45 mmol) and KL^{Br} (10.0 g, 17.45 mmol) in *N,N*-dimethylformamide (50 mL) was heated at 100 °C for 4 h. The volume of the reaction mixture was reduced to 25 mL, and it was then poured into a stirred, aqueous solution

(28) Lucas, H. J.; Kennedy, E. R. *Org. Synth.* **1955**, *3*, 482.

of tetraethylammonium chloride (4.0 g in 40 mL). After the mixture was stirred for 30 min, a yellow solid was filtered off and washed well with water. The wet solid was dissolved in hot acetonitrile (200 mL), and water (300 mL) was slowly added to precipitate the yellow, crystalline product which was isolated by filtration, washed with 1/1 acetonitrile/water (20 mL), methanol (10 mL), and ether (30 mL), and dried in vacuo. Yield: 8.65 g, 53%.

Anal. Calcd for $C_{26}H_{39}BBr_3N_7O_3W$: C, 33.51; H, 4.22; N, 10.52, Br, 25.72. Found: C, 33.45; H, 4.20; N, 10.48; Br, 25.82. IR (MeCN): ν(CO) 1885, 1752 cm^{-1}. IR (KBr): ν(CO) 1880, 1744, ν-(BH) 2550, ν(CN) 1531 cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 1.18 (tt, 12H, $^3J_{HH}$ 7 Hz, $^3J_{NH}$ 2 Hz, N(CH$_2$CH_3)$_4^+$), 2.34 (s, 9H, 3 × CH_3 of L^{Br}), 2.50 (s, 9H, 3 × CH_3 of L^{Br}), 3.12 (q, 8H, $^3J_{HH}$ 7 Hz, N(CH_2CH$_3$)$_4^+$).

L^{Br}WBr(CO)$_3$. A mixture of NEt$_4$[L^{Br}W(CO)$_3$] (1.0 g, 1.07 mmol) in acetonitrile (30 mL) was treated with Br$_2$ (0.06 mL, 1.16 mmol) and then stirred at room temperature for 15 min. The mixture was then reduced to dryness, and the residue was purified by column chromatography on silica using 1/1 dichloromethane/*n*-hexane as eluent. The compound was recrystallized from dichloromethane/*n*-hexane as orange crystals. Yield: 0.50 g, 53%.

Anal. Calcd for $C_{18}H_{19}BBr_4N_6O_3W$: C, 24.52; H, 2.17; N, 9.53; Br, 36.25. Found: C, 24.64; H, 2.19; N, 9.61; Br, 36.35. ^{13}C{^{1}H} NMR (CDCl$_3$): At 30 °C, δ 11.70, 15.89 (CH$_3$); 97.43 (4-*C*); 143.63, 151.27 (*C*CH$_3$); 231.15 br (*C*O). At −60 °C, δ 11.73, 12.34, 15.13, 15.81 (CH$_3$); 97.03 (4-*C*); 143.36, 146.15, 149.51, 150.64 (*C*CH$_3$); 227.05 br, 240.60 br (*C*O).

Alternative Syntheses of LWBr(CO)$_3$ and L^{Br}WBr(CO)$_3$. A solution of Br$_2$ (0.15 mL, 2.88 mmol) in acetonitrile (20 mL) was added dropwise over a period of 15 min to a suspension of NEt$_4$[LW(CO)$_3$] (2.00 g, 2.88 mmol) in acetonitrile (30 mL). The reaction mixture was allowed to stir for 30 min and then reduced to dryness in vacuo. The residue was dissolved in acetonitrile (30 mL), and methanol was added to precipitate crystals, which were isolated by filtration, washed with methanol, and dried under vacuum. The product (yield ca. 0.8 g) was a mixture of variable proportions (typically around 1:1 using the above conditions) of LWBr(CO)$_3$ and L^{Br}WBr(CO)$_3$. The compounds were separated by column chromatography on silica using 1/1 dichloromethane/*n*-hexane as eluent. They were identified by spectral comparisons with authentic samples prepared as above.

LWI(CO)$_3$. The method of Feng et al.[15] was modified as follows: A suspension of NEt$_4$[LW(CO)$_3$] (3.0 g, 4.31 mmol) and iodine (1.10 g, 4.31 mmol) in acetonitrile (20 mL) was stirred at room temperature for 30 min. Methanol (10 mL) was then added and the solution stirred for a further 10 min. The dark brown crystalline solid was filtered off, washed with cold methanol (5 mL), and dried in vacuo. Yield: 2.25 g, 75%. Spectroscopic data for this compound have been reported.[15]

NEt$_4$[L^{Pr}W(CO)$_3$]. The compound was prepared by modification of the method of Caffyn et al.[29] A suspension of W(CO)$_3$(MeCN)$_3$ (2.45 g, 6.26 mmol) and KL^{Pr} (2.37 g, 6.26 mmol) in acetonitrile (40 mL) was stirred for 15 h at room temperature. The volume of the mixture was then reduced to 20 mL, and the dark orange mixture was poured into a vigorously stirred aqueous solution of NEt$_4$Cl (5.0 g in 50 mL). The aqueous mixture was washed with two portions (50 mL) of dichloromethane, and the separated and combined organic fractions were enriched with diethyl ether to yield "red" crystals. After cooling of the mixture at −4 °C for several hours, the crystals were isolated by filtration and washed with *cold* methanol until the washings were colorless. The yield of yellow crystals was 1.66 g, 38%. The properties of the compound were identical with those reported previously.[29]

L^{Pr}WI(CO)$_3$. A solution of NEt$_4$[L^{Pr}W(CO)$_3$] (1.0 g, 1.36 mmol) and iodine (0.35 g, 1.38 mmol) in acetonitrile (10 mL) was stirred in air for 15 min. The brown crystalline solid was filtered off, washed with cold methanol (3 mL), and dried in vacuo. Yield: 0.62 g, 64%. This complex is more susceptible to aerial decomposition than LWI-(CO)$_3$.

Anal. Calcd for $C_{21}H_{28}BIN_6O_3W$: C, 34.36; H, 3.85; N, 11.45. Found: C, 34.40; H, 3.80; N, 11.55.

LWX(CO)$_2$. A suspension of LWX(CO)$_3$ in acetonitrile (10−15 mL/g of tricarbonyl) was heated to 80 °C for 30 min. After this period, the mixture was allowed to briefly cool and the pale brown crystalline solid was filtered off, washed with acetonitrile (2 mL), and dried in vacuo.

X = Cl. Yield: 83%. Anal. Calcd for $C_{17}H_{22}BClN_6O_2W$: C, 35.66; H, 3.87; N, 14.68; Cl, 6.19. Found: C, 35.58; H, 3.89; N, 14.62; Cl, 6.21.

X = Br. Yield: 80%. Anal. Calcd for $C_{17}H_{22}BBrN_6O_2W$: C, 33.09; H, 3.43; N, 13.62. Found: C, 33.42; H, 3.55; N, 13.58. Effective magnetic moment: Faraday method, μ_{eff} = 1.15 μ_B.

X = I. Yield: 78%. Anal. Calcd for $C_{17}H_{22}BIN_6O_2W$: C, 30.75; H, 3.34; N, 12.66. Found: C, 31.57; H, 3.40; N, 12.84. Effective magnetic moment: Evans method (in 99.8% CDCl$_3$/0.2% CHCl$_3$ at 294 K), μ_{eff} = 1.15 μ_B; Faraday method, μ_{eff} = 1.15 μ_B. Molar mass (VPO) (5.873 mg/mL in CH$_2$Cl$_2$): 620 g·mol^{-1}.

L^{Br}WBr(CO)$_2$. A suspension of L^{Br}WBr(CO)$_3$ (0.35 g, 0.40 mmol) in acetonitrile (10 mL) was heated at 70 °C for 1 h. The dark brown crystalline solid was filtered off, washed with acetonitrile (2 mL), and dried in vacuo. Yield: 0.28 g, 82%.

Anal. Calcd for $C_{17}H_{19}BBr_4N_6O_2W$: C, 23.91; H, 2.24; N, 9.84. Found: C, 23.78; H, 2.23; N, 9.81. Effective magnetic moment: Faraday method, μ_{eff} = 1.16 μ_B.

L^{Br}WBr(MeCN)(CO). A solution of L^{Br}WBr(CO)$_3$ (0.4 g, 0.45 mmol) in acetonitrile (25 mL) was refluxed for 1 h. The volume of the solvent was reduced to ca. 5 mL, and the olive green solid was isolated by filtration and washed with cold acetonitrile (2 mL). Yield: 0.20 g, 51%.

Anal. Calcd for $C_{18}H_{22}BBr_4N_7OW$: C, 24.95; H, 2.56; N, 11.31. Found: C, 24.96; H, 2.68; N, 11.16. IR (KBr): ν(BH) 2563, ν(CO) 1898, ν(C≡N) 1688, ν(CN) 1526 cm^{-1}. IR (CH$_2$Cl$_2$): ν(CO) 1915, ν(C≡N) 1702 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.85, 2.40, 2.48, 2.50, 2.55, 2.72 (s, 6 × 3H, 6 × CH_3 of L^{Br}), 3.94 (s, 3H, CH_3 of MeCN). ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 11.61, 12.05, 12.17, 13.66, 15.97, 16.85 (s, 6 × CH$_3$ of L^{Br}), 22.25 (s, CH$_3$ of MeCN), 98.21, 98.34, 98.42 (s, 3 × *C*Br of L^{Br}), 142.03, 143.46, 145.79, 150.78, 153.07, 153.34 (s, 6 × *C*Me of L^{Br}), 207.45 ($^1J_{WC}$ 26 Hz, C≡N of MeCN), 225.15 ($^1J_{WC}$ 158 Hz, *C*O). Electronic spectrum (CH$_2$Cl$_2$): 745 (90), 590 (200), 450 nm (ϵ 260 M^{-1}·cm^{-1}).

LW(CO)$_3$. A mixture of NEt$_4$[LW(CO)$_3$] (4.0 g, 5.75 mmol) and I$_2$ (0.73 g, 2.9 mmol) in acetonitrile (50 mL) was heated with stirring at ca. 70 °C for 2 h. The reaction mixture was allowed to cool, and the product was filtered off, washed with acetonitrile and then ether, and dried in vacuo. Yield: 2.9 g, 90%. The spectral properties of the compound were identical with those previously reported.[30]

Crystal Data. Dark brown crystals of L^{Pr}WI(CO)$_3$·MeOH were grown anaerobically by slow diffusion of methanol into a saturated 1,2-dichloroethane solution of the complex, and dark yellow crystals of L^{Br}WBr(MeCN)(CO) were grown by slow diffusion of *n*-hexane into a saturated dichloromethane solution of the complex. The crystals were air-stable and were not protected from the atmosphere during data collection; crystals of L^{Pr}WI(CO)$_3$·MeOH and L^{Br}WBr(MeCN)(CO) showed 6% and 2% deteriorations in reflection intensity, respectively. Intensity data were collected using an Enraf-Nonius CAD-4MachS single-crystal X-ray diffractometer using the ω:2θ scan method, with Mo Kα radiation (graphite crystal monochromator, λ = 0.710 73 Å) at 293(1) K. Accurate values of the unit cell parameters and crystal orientation were obtained by a least-squares procedure from the angular settings of 25 carefully centered reflections. Crystallographic data are summarized in Table 1.

Structure Solutions and Refinements. L^{Pr}WI(CO)$_3$·MeOH. The structure was solved by using a combination of direct methods and difference synthesis.[31,32] The iodine atom and one of the CO molecules were distributed over two of the positions of the capped trigonal face.

(29) Caffyn, A. J. M.; Feng, S. G.; Dierdorf, A.; Gamble, A. S.; Eldredge, P. A.; Vossen, M. R.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 2842.

(30) Philipp, C. C.; White, P. S.; Templeton, J. L. *Inorg. Chem.* **1992**, *31*, 3825.

(31) Sheldrick, G. M. SHELXS-86, Program for Crystal Structure Solution. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

Table 1. Crystallographic Data

	$L^{Pr}WI(CO)_3 \cdot MeOH$	$L^{Br}WBr(MeCN)(CO)$
formula	$C_{22}H_{32}BIN_6O_4W$	$C_{18}H_{22}BBr_4N_7OW$
fw	766.10	866.73
space group	$Pbca$	$C2/c$
a, Å	11.779(2)	22.245(4)
b, Å	15.975(4)	19.077(4)
c, Å	29.476(3)	15.639(3)
β, deg		128.61(2)
V, Å^3	5547(2)	5186(2)
Z	8	8
ρ_{calc}, g·cm^{-3}	1.835	2.220
R^a	0.0379	0.0515
$R_w{}^b$	0.0948	0.1207

^{a} For $I > 2\sigma(I)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} For all data, $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Both components of these three atoms were included in the refinement, with the interatomic separations of the minor component restrained to those observed for the major component. All hydrogen atoms were found in the difference maps and were constrained at geometrical estimates using the riding model. Full-matrix least-squares refinement on F^2, using all data, was carried out with anisotropic displacement parameters applied to each of the non-hydrogen atoms, except for the minor components of the disordered I, C, and O atoms. The refinement converged with R [$I > 2\sigma(I)$] and wR (all data) of 0.0379 and 0.0948, respectively. The weighting scheme employed was of the type $w = 1/[\sigma^2(F_o^2) + (0.0433P)^2 + 7.3180P]$, where $P = (F_o^2 + 2F_c^2)/3$. The final occupancy factors of the major and minor components of the I, C, and O atoms were 0.920(2) and 0.080(2), respectively. In the final difference map the maximum and minimum peak heights were 1.60 and -1.24 e·Å^{-3}, close to the iodine atom.
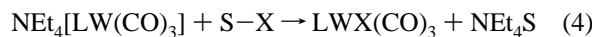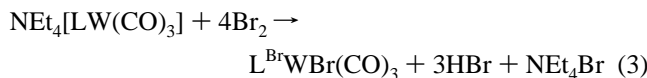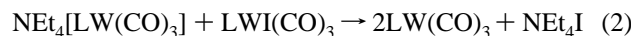
$L^{Br}WBr(MeCN)(CO)$. The structure was solved using a combination of Patterson map, direct methods, and difference syntheses.[31,32] Full-matrix least-squares refinement on F^2, using all data, was carried out with anisotropic displacement parameters applied to each of the non-hydrogen atoms, with $R = 0.057$. At this point peaks of about 1.5 e·Å^{-3} were found around the CO and MeCN ligands, suggesting that the Br, CO, and MeCN ligands were disordered over more than one position. It was possible to include the bromine distributed over two positions, with a variable site occupancy factor, but including the minor components of the CO and MeCN was not possible. All hydrogens were found in the difference map and were constrained at geometrical estimates using the riding model. The refinement converged with R [$I > 2\sigma(I)$] and wR (all data) of 0.0515 and 0.1207, respectively. The weighting scheme employed was of the type $w = 1/[\sigma^2(F_o^2) + (0.0561P)^2 + 31.66P^2]$. The final relative occupancies for the bromine atom at the two sites were 0.931(4) and 0.069(4). In the final difference map the maximum and minimum peak heights were 1.70 and -0.99 e·Å^{-3}, respectively, both close to the tungsten atom.

The atomic scattering factors of all atoms were taken from the *International Tables for Crystallography*;[33] corrections were made for anomalous dispersion. Calculations were carried out on a Vaxstation 4000VLC computer system. The program ORTEP[34] was employed in the preparation of Figures 1 and 4.

Results and Discussion

Tricarbonyl Complexes. Syntheses. The tricarbonyl complexes are prepared by oxidative halogenation of NEt$_4$[LW-(CO)$_3$]. Modification of the method of Feng et al.,[15] which involves the reaction of NEt$_4$[LW(CO)$_3$] with 1 equiv of I$_2$, permits the convenient synthesis of LWI(CO)$_3$ under aerobic

conditions (eq 1). Interestingly, the use of 0.5 equiv of I$_2$ results

$$NEt_4[LW(CO)_3] + I_2 \rightarrow LWI(CO)_3 + NEt_4I \quad (1)$$

$$NEt_4[LW(CO)_3] + LWI(CO)_3 \rightarrow 2LW(CO)_3 + NEt_4I \quad (2)$$

$$NEt_4[LW(CO)_3] + 4Br_2 \rightarrow$$
$$L^{Br}WBr(CO)_3 + 3HBr + NEt_4Br \quad (3)$$

$$NEt_4[LW(CO)_3] + S-X \rightarrow LWX(CO)_3 + NEt_4S \quad (4)$$

$$(X = Br, Cl)$$

in the formation of LW(CO)$_3$[30] in almost quantitative yield. The iodo tricarbonyl complex is initially formed (eq 1) but reacts with starting material to form the final product according to eq 2. Addition of further I$_2$ converts LW(CO)$_3$ to LWI(CO)$_3$. Direct reaction of NEt$_4$[LW(CO)$_3$] and LWI(CO)$_3$ also results in the formation of LW(CO)$_3$. These reactions, which occur at room temperature but are noticeably faster at higher temperatures, provide a new and convenient route to LW(CO)$_3$. The reaction of NEt$_4$[L^{Pr}W(CO)$_3$] with I$_2$ produces good yields of L^{Pr}WI(CO)$_3$.

Electrophilic bromination of the pyrazole rings of L (eq 3) complicates the reaction of NEt$_4$[LW(CO)$_3$] with 1 equiv of Br$_2$, producing mixtures of LWBr(CO)$_3$ and L^{Br}WBr(CO)$_3$. Reaction of NEt$_4$[LW(CO)$_3$] with 4 equiv of Br$_2$ still produces some LWBr(CO)$_3$ possibly due to deactivation of L by competitive bromination at tungsten. The 4-bromination of all three pyrazole rings of L is a notable feature of the side reaction. Mixtures of LWBr(CO)$_3$ and L^{Br}WBr(CO)$_3$ may be separated by column chromatography, or the compounds may be individually prepared. Reaction of NEt$_4$[LW(CO)$_3$] or LW(CO)$_3$ with *N*-bromosuccinimide results in the formation of LWBr(CO)$_3$. Likewise, reaction of NEt$_4$[L^{Br}W(CO)$_3$] with Br$_2$ or *N*-bromosuccinimide produces L^{Br}WBr(CO)$_3$. Complete reaction is achieved using only 1 equiv of *N*-bromosuccinimide, and the generation of tetraethylammonium succinimide[35] is implicated (eq 4, S = succinimide). A radical mechanism is likely in the reaction of LW(CO)$_3$ and *N*-bromosuccinimide. An analogous reaction using *N*-chlorosuccinimide provides a clean and efficient synthesis of the chloro complex LWCl(CO)$_3$ (eq 4). Reaction of NEt$_4$[LW(CO)$_3$] with stoichiometric amounts of PhICl$_2$ also yields LWCl(CO)$_3$, but some LW(CO)$_3$ is generally formed (this can be minimized at low temperature). Since [LW(CO)$_3$]$^-$ and LWCl(CO)$_3$ do not react to form LW(CO)$_3$, the formation of the radical is likely to result from a side reaction of [LW(CO)$_3$]$^-$ and PhICl$_2$. The radical reacts with PhICl$_2$ to form LWCl(CO)$_3$. The chloro and bromo complexes are orange, and the iodo complexes are dark brown. All the complexes are diamagnetic, moderately air-sensitive (Cl > Br > I), crystalline materials that are readily soluble in chlorinated hydrocarbons, acetonitrile, and tetrahydrofuran but insoluble in alcohols, diethyl ether, and hydrocarbon solvents. Finally, the complexes react with AgNO$_3$ in acetonitrile to produce a yellow species, presumably [LW(CO)$_3$(MeCN)]$^+$, exhibiting ν(CO) bands at 2053 and 1963 cm^{-1} in solution. The iodo complex reacts instantly,[15] the bromo complex over a period of minutes, and the chloro complex over a period of hours. The rate or degree of halide dissociation from the [LW(CO)$_3$]$^+$ center therefore follows the order I > Br > Cl.

(32) Sheldrick, G. M. *SHELXL-93. Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.
(33) *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993; Vol. C: (a) p 200; (b) p 219; (c) p 500.
(34) Johnson, C. K. *ORTEPII, Fortran Thermal Ellipsoid Plot Program*; Report ORNL-5138; Oak Ridge National Laboratories: Oak Ridge, Tn, 1976.

(35) Barry, J. E.; Finkelstein, M.; Moore, W. M.; Ross, S. D.; Eberson, L.; Jönsson, L. *J. Org. Chem.* **1982**, *47*, 1292.

Table 2. Infrared Data (cm^{-1})

compd	ν(CO) (CH$_2$Cl$_2$)	ν(CO) (KBr)	ν(BH)^a	ν(CN)^a
LWCl(CO)$_3$	2027, 1936,^{b} 1912	2016, 1929, 1899	2550	1542
LWBr(CO)$_3$	2025, 1933,^{b} 1915	2022, 1913, 1897	2560	1546
L^{Br}WBr(CO)$_3$	2024, 1931,^{b} 1910	2029, 1930, 1920	2566	1533
LWI(CO)$_3$	2020, 1920	2012, 1915, 1872	2550	1545
L^{Pr}WI(CO)$_3$	2010, 1925	2018, 1910, 1908	2509	1510
LWCl(CO)$_2$	1925, 1834 (γ 47°)^c	1919, 1822	2550	1540
LWBr(CO)$_2$	1937, 1841 (γ 48°)^c	1933, 1826	2550	1540
L^{Br}WBr(CO)$_2$	1945, 1857 (γ 47°)^c	1936, 1841	2560	1526
LWI(CO)$_2$	1946, 1845 (γ 46°)^c	1927, 1817	2550	1540

^{a} KBr disk. ^{b} Unresolved shoulder. ^{c} The equation $\tan^2\gamma = I(a')/I(a'')$ was used to calculate the angle γ.[38] The C−W−C bond angle is equal to $(180 - 2\gamma)°$.

Spectroscopic Characterization. The infrared spectra of the complexes contain bands due to the carbonyl ligands, as well as the fingerprint bands of the appropriate pyrazolylborate ligand (Table 2). A single ν(CN) band in the spectrum of L^{Pr}WI-(CO)$_3$ is indicative of the presence of L^{Pr} rather than the isomeric hydrobis(3-isopropylpyrazol-1-yl)(5-isopropylpyrazol-1-yl)borate ligand.[36] The solution and solid-state IR spectra of LWCl-(CO)$_3$, LWBr(CO)$_3$, and L^{Br}WBr(CO)$_3$ exhibit three ν(CO) bands, a sharp band at ca. 2020 cm^{-1} and two stronger, overlapping bands in the 1930−1900 cm^{-1} region; this is consistent with molecular C_s symmetry in both phases (lower symmetry is not consistent with the NMR data; vide infra). Three ν(CO) bands are also observed in the solid-state IR spectra of LWI(CO)$_3$ and L^{Pr}WI(CO)$_3$, consistent with the carbonyl-capped octahedral (CO$_h$-CO$_{ax}$) structure established for L^{Pr}WI-(CO)$_3$ (vide infra). However, the solution IR spectra of these complexes exhibit only two ν(CO) bands, implying either a 3:3:1 iodide-capped octahedral (CO$_h$-I$_{ax}$, C_{3v}) structure on the IR time scale (A$_1$ and E vibrations) or coincidental degeneracy of the A″ and low energy A′ vibrations under C_s symmetry. Since L^{Pr}WI(CO)$_3$ possesses C_s symmetry in solution (by NMR), it is clear that its IR spectrum results from the degeneracy of the A″ and A′ vibrations. For fluxional LWX(CO)$_3$ and L^{Br}WBr-(CO)$_3$, the observation of species with C_s symmetry at −80 °C (by NMR) implies a static structure having C_s symmetry. Therefore, degeneracy of A′ and A″ ν(CO) modes must again be invoked to explain the observation of only two solution IR ν(CO) bands. The solution IR spectra of [LW(CO)$_3$(PR$_3$)]$^+$ (PR$_3$ = PMe$_2$Ph, PMe$_3$, PEt$_3$),[30] examples of bona fide 3:3:1 phosphine-capped octahedral complexes, exhibit two ν(CO) bands, but the A$_1$ mode is weak and noticeably broad compared to the corresponding band in the tricarbonyl iodide complexes.

Variable-temperature ^{1}H NMR spectra of LWX(CO)$_3$ (Table 3) are consistent with fluxional behavior. The room-temperature spectrum of LWCl(CO)$_3$ exhibits four somewhat broadened methyl resonances with an intensity ratio of 3:3:6:6, consistent with a C_s molecule undergoing slow exchange. These resonances sharpen and shift only marginally as the temperature is lowered; only one methine resonance is observed at all temperatures. The spectra of LWBr(CO)$_3$ and L^{Br}WBr(CO)$_3$ exhibit a sharp signal at δ ca. 2.47 and two very broad signals at δ ca. 2.3 and 2.1. These resonances also sharpen and shift at lower temperature to produce spectra indicative of molecular C_s symmetry. The spectra of LWI(CO)$_3$ exhibit similar behavior except that only two signals, one sharp and the other broad, are observed at room temperature.[15] At higher temperatures the

(36) (a) Xiao, Z.; Bruck, M. A.; Doyle, C.; Enemark, J. H.; Grittini, C.; Gable, R. W.; Wedd, A. G.; Young, C. G. *Inorg. Chem.* **1995**, *34*, 5950. (b) Young, C. G.; Laughlin, L. J.; Colmanet, S.; Scrofani, S. D. B. *Inorg. Chem.* **1996**, *35*, 5368.

Table 3. Proton NMR Data^a

compd (temp, °C)	δ (no. of protons)	
	CH_3	CH
LWCl(CO)$_3$ (30)	2.11 (3H), 2.35 (6H)	5.93 (3H)
	2.43 (6H), 2.45 (3H)	
LWCl(CO)$_3$ (−80)	2.06 (3H), 2.32 (6H)	5.97 (3H)
	2.40 (6H), 2.42 (3H)	
LWBr(CO)$_3$ (30)	2.12 (3H), 2.36 (6H)	5.95 (3H)
	2.44 (9H)	
LWBr(CO)$_3$ (−80)	2.09 (3H), 2.33 (6H)	5.97 (1H)
	2.42 (9H)	5.98 (2H)
L^{Br}WBr(CO)$_3$ (30)	2.17 (3H), 2.37 (6H)	
	2.47 (9H)	
L^{Br}WBr(CO)$_3$ (−80)	2.13 (3H), 2.33 (6H)	
	2.47 (9H)	
LWI(CO)$_3$ (30)^b	2.34 (9H), 2.49 (9H)	6.03 (3H)
LWI(CO)$_3$ (−80)^b	2.11 (3H), 2.31 (6H)	6.01 (1H)
	2.40 (3H), 2.47 (6H)	6.04 (2H)
L^{Pr}WI(CO)$_3$ (30)	1.20 (6H), 1.25 (6H)	6.2 (3H)
	1.30 (6H)	7.65 (2H)
	2.75 (1H),^{c} 3.16 (2H)^c	7.75 (1H)
LWCl(CO)$_2$ (30)	8.69 (3H), 14.43 (6H)	2.27 (1H)
	16.90 (3H), 20.82 (3H)	8.12 (2H)
LWBr(CO)$_2$ (30)	9.61 (6H), 15.89 (6H)	1.47 (1H)
	18.41 (3H), 21.70 (3H)	8.24 (2H)
L^{Br}WBr(CO)$_2$ (30)	11.39 (6H), 19.77 (6H)	
	23.05 (3H), 27.27 (3H)	
LWI(CO)$_2$ (30)	10.31 (6H), 16.66 (6H)	0.79 (1H)
	19.68 (3H), 21.00 (3H)	8.21 (2H)

^{a} In CDCl$_3$ at 30 °C, in CD$_2$Cl$_2$ at −80 °C. ^{b} From ref 15. ^{c} Resonances due to CHMe$_2$ groups of L^{Pr}.

spectra of all the complexes are consistent with effective C_{3v} symmetry at the fast-exchange limit. The behavior described above may be interpreted in terms of halide exchange (over three sites) in CO$_h$-CO$_{ax}$ complexes; the relative rates would appear to be in the order Cl < Br < I, the larger halides inducing a greater degree of stereochemical lability. This behavior is reflected in the ^{13}C NMR spectra (Experimental Section); the observation of broad carbonyl resonances at low-temperature suggests that a fluxional process involving the carbonyl ligands persists even when halide site-exchange has been arrested. Mixtures of LWBr(CO)$_3$ and L^{Br}WBr(CO)$_3$ are revealed by the presence of two sharp resonances at δ ca. 2.47. At room temperature, the ^{1}H NMR spectrum of L^{Pr}WI(CO)$_3$ displays three overlapping doublet methyl resonances, a pair of broadened multiplets due to the *i*-Pr methine groups (1:2 intensity ratio), a single broad resonance due to the 4-methine protons, and two 5-methine resonances having an intensity ratio of 1:2. The spectrum is indicative of molecular C_s symmetry.

Structure of L^{Pr}WI(CO)$_3$. Seven-coordinate L^{Pr}WI(CO)$_3$ exhibits a 3:3:1 structure having approximate C_s symmetry. A view of the molecule is given in Figure 1, and selected bond distances and angles are presented in Table 4. The tungsten center is coordinated by a facially tridentate L^{Pr} ligand, three carbonyl ligands, and an iodide ligand. The mirror plane is defined by C(2), O(2), W, I, B, and the ring containing N(11); the C(2), W, I and N(11) atoms are planar with a maximum displacement of only 0.006(1) Å for W. The coordination sphere closely approaches a capped octahedral geometry with an axial carbonyl ligand. The (distorted) octahedron is defined by atoms C(1), C(3), N(n1), and I; the capping carbonyl ligand lies close to the pseudo-3-fold axis projecting out of the face defined by C(1), C(3), and I. The idealized CO$_h$-CO$_{ax}$ geometry is compared to the real structure in Figure 2a. The non-carbon atoms are displaced an average of 0.03 Å from their idealized CO$_h$ positions, while the other donor atoms are displaced from idealized positions as follows (Δ = separation of real and

Table 4. Selected Bond Distances (Å) and Angles (deg) for $L^{Pr}WI(CO)_3$

W−I	2.8494(7)	W−C(1)	1.985(7)	W−C(2)	1.965(7)
W−C(3)	1.985(4)	W−N(11)	2.224(5)	W−N(21)	2.250(5)
W−N(31)	2.248(5)	C(1)−O(1)	1.116(8)	C(2)−O(2)	1.167(8)
C(3)−O(3)	1.124(4)				
I−W−C(1)	111.6(2)	I−W−C(2)	69.1(2)	I−W−C(3)	113.6(2)
C(1)−W−C(2)	71.5(3)	C(1)−W−C(3)	102.4(3)	C(2)−W−C(3)	70.6(3)
I−W−N(11)	156.14(13)	I−W−N(21)	79.61(14)	I−W−N(31)	79.94(14)
C(1)−W−N(11)	82.1(2)	C(1)−W−N(21)	163.0(2)	C(1)−W−N(31)	83.7(2)
C(2)−W−N(11)	134.7(2)	C(2)−W−N(21)	125.3(2)	C(2)−W−N(31)	128.3(2)
C(3)−W−N(11)	80.4(3)	C(3)−W−N(21)	83.4(3)	C(3)−W−N(31)	160.8(3)
N(11)−W−N(21)	83.2(2)	N(11)−W−N(31)	82.5(2)	N(21)−W−N(31)	86.0(2)
W−C(1)−O(1)	178.1(6)	W−C(2)−O(2)	174.7(6)	W−C(3)−O(3)	177.2(10)
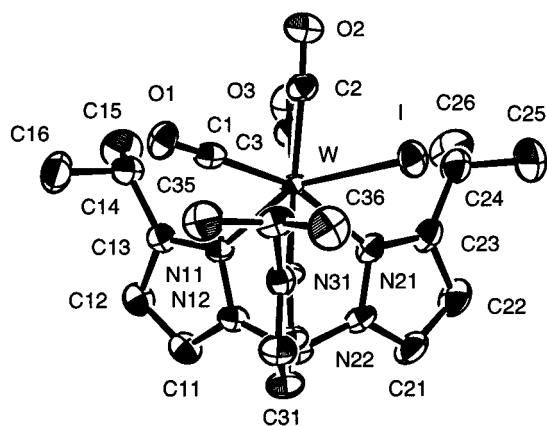
Figure 1. Molecular structure and numbering scheme for $L^{Pr}WI(CO)_3$. For clarity, the B, N(32), and C(32)−C(34) atoms are unlabeled and hydrogen atoms have been omitted. The probablility ellipsoids are drawn at the 35% level.
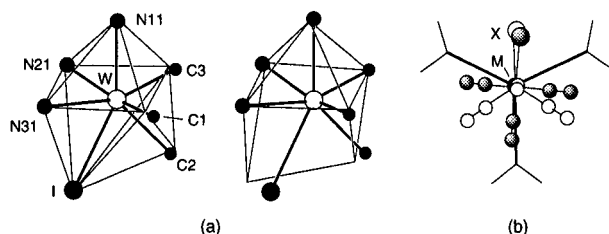
Figure 2. (a) Comparisons of the structure of the coordination sphere of $L^{Pr}WI(CO)_3$ with the idealized CO_h-CO (left) and CTP-N_{ax} (right) geometries. The idealized polyhedra, generated using appropriate polar angles[11] and real metal−donor distances, are superimposed on two identical views of the real coordination sphere. (b) Superposition of the structures of $L^{Pr}WI(CO)_3$ and $(HB(pz)_3)MoBr(CO)_3$. Only the metal (black) and carbonyl and halide atoms, for the former complex as open circles and for the latter as shaded circles, are shown. The bolded Y-shaped spokes represent the positions of the isopropylpyrazole rings of L^{Pr}, which coincide closely with those of the pyrazole rings of $HB(pz)_3^-$.

idealized positions): $\Delta_{C(1)} = 0.25$ Å, $\Delta_{C(2)} = 0.20$ Å, and $\Delta_{C(3)} = 0.20$ Å. The δ' angles for $L^{Pr}WI(CO)_3$, as defined by Muetterties and Guggenberger,[37] are $\delta'_1 = 15.2°$, $\delta'_2 = 10.2°$, and $\delta'_3 = 28.8°$; these compare reasonably well with the δ' angles expected for an idealized CO_h geometry, $\delta'_1 = \delta'_2 = \delta'_3 = 16.2°$, the differences being due to the displacement of the carbonyl carbon atoms, especially C(2), from their idealized positions. As expected, atoms I, C(1), and C(3) are splayed away from the capping ligand. The W atom lies 0.747(4) Å out of the plane defined by I, C(1), and C(3) and 1.424(3) Å

(37) (a) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748. (b) An important correction relating to seven-coordinate structures can be found in: Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1977**, *99*, 3893.

out of the plane of the opposite face defined by the three N(n1) atoms; these two faces are parallel with a dihedral angle of just 1.3(3)°. This distortion is reflected in the angles subtended with the W··B axis, W−I 74.7°, W−C(1) 67.2°, W−C(3) 68.7°, and W−$N_{average}$ 129.5°, and the average trans I/C_{face}−W−N angle of 160°. The structure of $L^{Pr}WI(CO)_3$ is compared to the closest idealized capped trigonal prismatic (CTP) structure, with N(11) (the capping atom), W, I, and C(2) in a σ_v plane, in Figure 2a. The δ' angles for the CTP geometry, $\delta'_1 = \delta'_2 = 0°$, and $\delta'_3 = 41.5°$, differ substantially from those of the observed structure. The W−C distances lie in the range 1.965(7)−1.985(7) Å; although not statistically significant, the W−C(2) distance is the shortest of the three. The W−I distance is 2.8494(7) Å, and the W−N(n1) distances lie between 2.224(5) and 2.250(5) Å. Overall, the L^{Pr} ligand is coordinated very symmetrically to the tungsten center; there is one minor distortion reflected in the opening of the N(21)−W−N(31) angle (86.0(2)°) relative to the other two N−W−N angles (average 82.8°). The capping carbonyl ligand subtends a small angle (5.8°) to the W··B axis and is characterized by a W−C(2)−O(2) angle of 174.7(6)°. The other two carbonyl ligands are more linear, with W−C(1)−O(1) and W−C(3)−O(3) angles of 178.1(6) and 177.2(10)°, respectively. The pyrazole rings are planar, and each isopropyl group is symmetrically disposed with respect to the attached ring, with its methyl groups pointing away from the tungsten atom.

The structure of $(HB(pz)_3)MoBr(CO)_3$, which has been described in terms of CTP-Br_{ax} and CTP-N_{ax} geometries,[7,10] also closely approximates a CO_h-CO_{ax} structure. In this description, C(2) serves as the capping atom and the δ' angles are as follows: $\delta'_1 = 8.8°$, $\delta'_2 = 26.8°$, and $\delta'_3 = 11.1°$. The values are close to those observed for $L^{Pr}WI(CO)_3$. For the CTP-N_{ax} description, $\delta'_1 = 8.8°$, $\delta'_2 = 11.1°$, and $\delta'_3 = 26.8°$ compared to $\delta'_1 = \delta'_2 = 0°$ and $\delta'_3 = 41.5°$ for the idealized CTP geometry. Thus, the structures of $(HB(pz)_3)MoBr(CO)_3$ and $L^{Pr}WI(CO)_3$ are closely related and essentially differ in the sites occupied by the halide and tripodal N-donor ligands. A superposition of the tungsten and molybdenum complexes (Figure 2b) further highlights the similarities and differences in their structures. The metal−halide−pyrazolylborate fragments are very similar, but the arrangement of the carbonyl ligands is clearly different. This is principally a consequence of the steric influence of the pyrazole 3-substituents. For $(HB(pz)_3)MoBr(CO)_3$, the siting of the in-plane carbonyl ligand is permitted by a 3-H to carbonyl oxygen distance of 2.52 Å. If the in-plane carbonyl ligand of $L^{Pr}WI(CO)_3$ was to be similarly situated a methine H to carbonyl oxygen distance of only 1.30 Å would pertain; this steric conflict is clearly relieved by the adoption of the CO_h-CO_{ax} structure. Indeed, for complexes of this general type, the relative stabilities of the various geometrical isomers and the rates of the fluxional processes can be

rationalized in terms of the steric demands of the various pyrazolylborate ligands.

Dicarbonyl Complexes. Syntheses. The $LWX(CO)_3$ and $L^{Br}WBr(CO)_3$ complexes are unstable at elevated temperatures (>70 °C) and convert to the brown dicarbonyl complexes, $LWX(CO)_2$ and $L^{Br}WBr(CO)_2$, upon reflux in acetonitrile or tetrahydrofuran (eq 5). Solution infrared studies of the reaction

$$LWX(CO)_3 \rightleftharpoons LWX(CO)_2 + CO\uparrow \qquad (5)$$

$$LWX(CO)_2 + MeCN \rightleftharpoons LWX(MeCN)(CO) + CO\uparrow \qquad (6)$$

mixtures reveal the replacement of the $\nu(CO)$ bands of the tricarbonyl with those of the dicarbonyl (ca. 1930 and 1840 cm^{-1}), and the insoluble products are isolated simply by filtration. Prolonged reflux in acetonitrile leads to the formation of acetonitrile-$\kappa^2 N,C$ complexes, $LWX(MeCN)(CO)$ (eq 6);[22,23] consequently, reaction time is an important variable in the synthesis of the $LWX(CO)_2$ complexes. The dicarbonyl complexes readily react with carbon monoxide to re-form the tricarbonyl complexes, paralleling the carbon monoxide carrying behavior of many other Mo(II) and W(II) complexes (eq 5, reverse). Re-formation of the dicarbonyl complexes from the nitriles requires elevated temperatures, e.g., 55 °C in MeCN (eq 6, reverse). The mildly air-sensitive dicarbonyl complexes are readily soluble in chlorinated hydrocarbons and tetrahydrofuran but only sparingly soluble in acetonitrile, ethers, alcohols, and hydrocarbons. The complexes are decomposed by alcohols.

Physical and Spectroscopic Data. Although we have been unable to crystallographically characterize any of the dicarbonyl complexes, the following evidence supports their formulation as mononuclear cis-dicarbonyl species. For $LWI(CO)_2$, the molar mass determined by ebulliometry (630 g·mol^{-1}) is only 5% lower than the value calculated for the monomer (663 g·mol^{-1}). The two $\nu(CO)$ bands observed in solution and solid-state IR spectra (Table 2) can be assigned to the A′ and A″ modes of a cis-dicarbonyl fragment in a mononuclear complex of C_s symmetry. Under C_s symmetry, these modes would be Raman active and the observation of the low frequency $\nu(CO)$ band in Raman spectra supports a mononuclear formulation (the second Raman mode appears to have negligible intensity). Using the treatment described by Burdett,[38] the angle γ and the C−W−C bond angle can be calculated from the relative intensities of the two bands; acute C−W−C bond angles were observed in each case (Table 2). The complexes exhibit isotropically shifted ^{1}H NMR signals in the δ 0−30 region (Table 3) with resonance patterns indicative of molecular C_s symmetry in solution. At room temperature, all the dicarbonyl complexes exhibit very low solid-state and solution magnetic moments in the range 1.15−1.2 μ_B. The solid-state magnetic moments are temperature dependent and show deviations from Curie−Weiss behavior.

The electronic structures of the $LWX(CO)_2$ complexes, and related species,[14,39,40] are of considerable interest. Three bonding molecular orbitals (Figure 3) are generated upon combination of metal d_π and carbonyl π^* orbitals. The first is produced by overlap of the a′ $d_{x^2-y^2}$ orbital with the symmetry-adapted CO $\pi_{\parallel}^*$ orbitals in the xy plane (the y axis is perpendicular to the mirror plane, and the x axis bisects the C−W−C unit). The other two involve the symmetry-adapted CO $\pi_{\bar{v}}^*$ orbitals di-
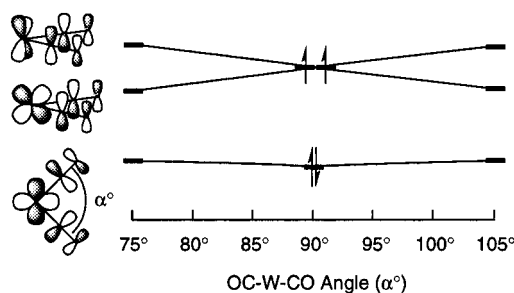
Figure 3. Frontier molecular orbitals and their relative energies as a function of C−W−C angle for $LWI(CO)_2$. Energies were derived from extended Hückel molecular orbital calculations.

rected along the z axis, of symmetry species a′ and a″, and the metal d_{xz} and d_{yz} orbitals. When the C−W−C angle is exactly 90°, these orbitals are degenerate. For more acute C−W−C angles, the a′ orbital combination will be lower in energy than the a″ orbital combination; for more obtuse angles, the energy ordering of these two orbitals will be reversed. However, for all realistic C−W−C angles the energy gap between these two orbitals is likely to be small. Templeton et al.[40] have described qualitatively similar results for the hypothetical complexes $[H_3W(NR_2)(CO)_2]^{2-}$ (R = H, Me), $[H_3W(EH)(CO)_2]^{2-}$ ($E =$ O, S), and $[H_3W(HCCH)(CO)_2]^-$, all of which feature a single-sided π-donor ligand bonded to a $[H_3W^{II}(CO)_2]^-$ fragment. These complexes are models for pyrazolylborate complexes such as $LW(NR_2)(CO)_2$, $LW(SR)(CO)_2$, and $LW(RCCR')(CO)_2$, prepared and studied by Templeton and others.[15−19] Importantly, single-sided π-donors in the xz plane stabilize the d_{yz} (or a″ MO) orbital through a π interaction involving the filled p_y orbital of the N-, E- or CC_π-donors. This interaction is enhanced by acute C−W−C angles (as low as 73°), and as a consequence of the substantial energy gap between the a′ and a″ MOs, low-spin (diamagnetic) complexes result. In the $LWX(CO)_2$ complexes under discussion, the halide ligand does not participate in significant π bonding with the metal. This is consistent with the calculated C−W−C angles (>84°) and the observed paramagnetism of the complexes, which results from near degeneracy of the previously mentioned a′ and a″ MOs. The unusually low, temperature-dependent magnetic susceptibilities of the compounds may be explained in terms of a singlet ground state and a thermally populated triplet excited state,[41] but a full description of the magnetic properties will require detailed magnetochemical and EPR studies.

Synthesis and Characterization of $L^{Br}WBr(MeCN)(CO)$. Further decarbonylation of $L^{Br}WBr(CO)_2$ results in the formation of $L^{Br}WBr(MeCN)(CO)$ (cf. eq 6). By virtue of the lower solubility of $L^{Br}WBr(MeCN)(CO)$ compared to $LWBr(MeCN)-$ (CO), the former may be isolated free of the latter even when mixtures of $L^{Br}WBr(CO)_2$ and $LWBr(CO)_2$ are heated in acetonitrile. In fact, the nitrile complex was first prepared in this manner and its characterization first alerted us to the bromination of the pyrazole rings.[18,24] The complex exhibits a single $\nu(CO)$ band at 1898 cm^{-1}, and NMR spectra are indicative of the presence of one isomer with C_1 symmetry. The acetonitrile methyl resonance appears at δ 3.94, consistent with the presence of a four-electron-donor acetonitrile-$\kappa^2 N,C$ ligand.[22−24] The crystal structure of $L^{Br}WBr(MeCN)(CO)$ confirmed the complete 4-bromination of L, which occurs at the first stage of the reaction sequence (eq 3). A view of the molecule, along with selected bond distances and angles, is given in Figure 4. The seven-coordinate complex contains a facially

(38) Burdett, J. K. *Inorg. Chem.* **1981**, *20*, 2607.

(39) Kubácek, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4320.

(40) Templeton, J. L.; Caldarelli, J. L.; Feng, S.-G.; Philipp, C. C.; Wells, M. B.; Woodworth, B. E.; White, P. S. *J. Organomet. Chem.* **1994**, *478*, 103.

(41) Figgis, B. N.; Lewis, J. *Prog. Inorg. Chem.* **1964**, *6*, 37.
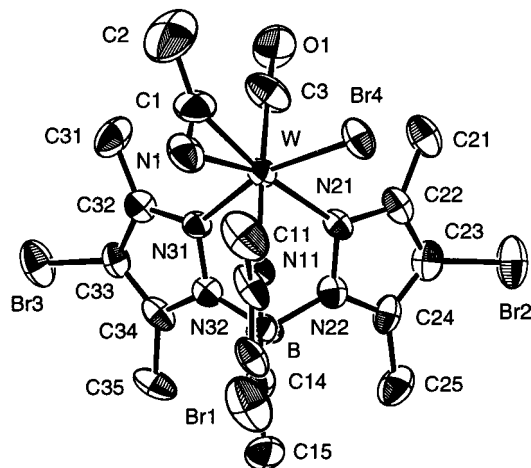
Figure 4. Molecular structure and numbering scheme for $L^{Br}WBr$-(MeCN)(CO). The hydrogen atoms have been omitted for clarity, and the probability ellipsoids are drawn at the 35% level. Selected distances and angles include the following: W–Br(4) 2.5509(14), W–C(1) 2.038(15), W–C(3) 1.88(2), W–N(1) 2.072(12), W–N(11) 2.259(8), W–N(21) 2.208(8), W–N(31) 2.152(8), C(1)–N(1) 1.10(2), C(3)–O(1) 1.16(2) Å; W–C(1)–N(1) 73.6(11), W–N(1)–C(1) 72.8(11), N(1)–C(1)–C(2) 136(2), N(1)–W–C(1) 30.9(5), W–C(3)–O(1) 174.5(15)°.

tridentate L^{Br} ligand, carbonyl and bromide ligands, and a side-on-bound acetonitrile-$\kappa^2 C,N$ ligand. A distorted octahedral structure pertains when the acetonitrile ligand is considered to occupy one coordination site. The non-hydrogen atoms of the W(MeCN)(CO) framework are very nearly planar, and there is a syn relationship between the nitrile methyl and metal carbonyl groups. The syn arrangement is sterically preferred but the orientation of the acetonitrile ligand with respect to the carbonyl ligand is dictated by π-back-bonding considerations.[22b] Due to the disorder, metric parameters (Figure 4) must be treated with caution. Structurally and spectroscopically, $L^{Br}WBr$-(MeCN)(CO) is closely related to recently reported LWX-(MeCN)(CO) complexes.[22–24]

Summary

Optimal syntheses and full characterization data are reported for the halocarbonyltungsten(II) complexes of L, viz. LWX-$(CO)_3$ and $LWX(CO)_2$, and selected L^{Br} and L^{Pr} complexes. Bromination of L attends the reaction of $NEt_4[LW(CO)_3]$ with Br_2, and it is likely that similar complications adversely effect closely related systems. The fluxional seven-coordinate tricarbonyl complexes possess ground-state carbonyl-capped octahedral structures with C_s symmetry. The crystal structure of $L^{Pr}WI(CO)_3$, which reveals a 3:3:1 carbonyl-capped octahedral structure, is the first available for tungsten complexes of this type. This complex possesses a close structural relationship to $(HB(pz)_3)MoBr(CO)_3$,[10] shown here to adopt an approximate capped octahedral structure. The six-coordinate, paramagnetic dicarbonyl complexes are octahedral and also possess C_s symmetry. They are identified as the immediate precursors of complexes such as $LWX(MeCN)(CO)$,[22,23] which in turn may be converted to carbonylthiotungsten(IV),[22,23] acylimidotungsten(IV),[42] and halocarbonyltungsten(III)[24] species. The work described provides a broad and solid foundation on which to further develop the organometallic and coordination chemistries of tungsten poly(pyrazolyl)borate compounds.

(42) Thomas, S.; Lim, P. J.; Gable, R. W.; Young, C. G. *Inorg. Chem.* **1998**, *37*, 590.