bipyramidal, with an equatorial plane comprised of S(1), S(2), and S(3) and S–Cu–O angles of 72.9 (2), 72.4 (2), and 75.9 (2)°, respectively. Further, the opposing Cu–S(4) bond is 2.351 (2) Å, longer than any of the other Cu–S bonds (2.311 Å average). An examination of the interatomic distances and angles around O(1) is also revealing. In addition to its interaction with Cu, O(1) is involved in a hydrogen bond to the hydroxyl hydrogen of the lattice methanol molecule. The position of this hydrogen atom was determined from a difference map and was allowed to refine freely. It is therefore possible to examine all of the angles around O(1), and these are listed in Table III. Although some of the esd's are necessarily large, a reasonable disposition in space is obtained. On the basis of these results it appears that the methoxyl oxygen is located in a potential energy well that imparts an apparent trigonal-bipyramidal geometry to the Cu(I). By contrast, the methoxyl oxygen in the other chelate ring exhibits no tendency to interact with Cu(I).

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Registry No. 3-OMe-1,5-DTCO, 86944-02-7; 3-OH-1,5-DTCO, 86944-00-5; Cu(3-OMe-1,5-DTCO)$_2$(ClO$_4$)$_2$, 91670-00-7; Cu(3-OMe-1,5-DTCO)$_2$ClO$_4$·CH$_3$OH, 91670-03-0.

Supplementary Material Available: Listings of interatomic distances, angles, hydrogen coordinates, anisotropic thermal parameters, and observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Ligand-Bridged Dimers. 2. Homobinuclear Derivatives of (Methylcyclopentadienyl)manganese Dicarbonyl[1]

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The solvent adducts $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2\cdot\text{S}$ (where S = diethyl ether, tetrahydrofuran), which can be prepared photochemically[3] as in eq 1, serve as useful intermediates for the

$$(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_3 \xrightarrow[\text{S}]{h\nu} (\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2\cdot\text{S} + \text{CO} \quad (1)$$

thermal syntheses of monosubstituted derivatives[4] of the tricarbonyl (eq 2). We have made use of this reactivity to extend

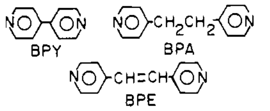
$$(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2\cdot\text{S} \xrightarrow[\text{S}]{\text{X}} (\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2\text{X} \quad (2)$$

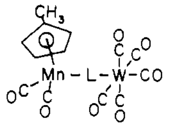
Table I. IR Spectroscopic Data[a]

compds	ν_{CO}, cm^{-1}
$(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_3$	2018 (m), 1932 (s)
$(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2\cdot\text{THF}$	1921 (s), 1848 (m)
$[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2]_2\text{BPA}$	1921 (s), 1850 (s)
$[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2]_2\text{BPY}$	1920 (s), 1852 (s)
$[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2]_2\text{BPE}$	1928 (s), 1850 (s)

[a] In THF solution.

our work[1] on the syntheses of ligand-bridged dimers. In this paper we present the synthesis and characterization of the ligand-bridged dimers of the general formula $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2]_2\text{L}$, where L = 4,4′-bipyridine (BPY), 1,2-bis(4-pyridyl)ethylene (BPE), and 1,2-bis(4-pyridyl)ethane (BPA). We view the characterization of these compounds as a natural prelude to the synthesis and characterization of the heteronuclear ligand-bridged dimers shown in I, whose photochemistries we hope eventually to be able to study. Compounds of the type shown in I should be especially interesting because of known differences in the spectra and photoreactivities of the mononuclear compounds W(CO)$_5$X[5] and $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2\text{X}$.[6]





I

Experimental Section

Materials and Reagents. The starting tricarbonyl, $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_3$, was obtained from Strem Chemicals and was distilled under vacuum and stored under argon prior to use. The ligands BPA and BPE were obtained from Aldrich and used without purification. The ligand BPY was obtained from Aldrich as the dihydrate and was purified by vacuum sublimation. All solvents were distilled from LiAlH$_4$, under argon. Solvents were transferred under argon with use of syringe techniques.

Photolyses were carried out with a 450-W Hanovia medium-pressure mercury vapor lamp that was housed in an Ace Glass quartz immersion well. The photolyses were performed at 0 °C and under a constant purge of argon. All of the products were handled under argon with use of standard Schlenk techniques, as well as in a minimum amount of dim red light.

Synthetic Procedures. The dimeric products were prepared by the general synthetic procedure in which the free ligand BPY, BPA, or BPE was reacted thermally in a dry THF solution of the solvent adduct $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2\cdot\text{THF}$. The THF adduct had to be freshly prepared but was not isolated. A specific example where L = BPY is typical of all syntheses.

$(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_3$, 0.6 mL (5.2 mmol), was photolyzed under argon, at 0 °C in previously distilled THF (270 mL) for 1 h or until an infrared spectrum showed complete conversion to the THF adduct (vide infra). A continuous stream of argon was bubbled through the solution during photolysis to purge carbon monoxide from the solution. During photolysis, the color changed from pale yellow to a deep burgundy characteristic of the solvent adduct, $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2\cdot\text{THF}$. The THF solution was then transferred via syringe to a flask containing BPY 0.52 g (3.2 mmol), which had previously been purged with argon. Thermal reaction for typically 2 h resulted in a color change to red (yellow when L = BPA, purple when L = BPE). Solvent was removed by distillation, and the solid product was purified by multiple recrystallizations from THF/hexane.

Yields were 40–60% depending on the ligand used. Anal. (Galbraith) Calcd for $[\text{CH}_3\text{C}_5\text{H}_4\text{Mn(CO)}_2]_2\text{N}_2\text{C}_{10}\text{H}_8$: C, 58.22; H, 4.14, N, 5.22. Found: C, 57.80; H, 4.22, N, 6.04. Calcd for

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Table II. ^{1}H NMR Spectroscopic Data[a]

compds	L ortho[b]	L meta[c]	L other	$-CH_3$[d]	Cp ring[e]
$(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$				1.93	4.73
BPA	8.47	7.22	3.00[f]		
$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]_2BPA$	8.50	7.09	2.94[f]	1.47	4.07, 4.43
BPY	8.97	7.74			
$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]_2BPY$	8.75	7.61		1.47	4.18, 4.46
BPE	8.59	7.56	7.51[g]		
$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]_2BPE$	8.66	7.43	7.59[g]	1.39	4.14, 4.49

[a] In deuterated THF; chemical shifts in ppm relative to Me_4Si. [b] Chemical shifts measured to the center of the downfield member of an aromatic doublet of multiplets and assigned to ring protons (of the bidentate ligand L) ortho to the ring nitrogens. [c] Chemical shifts measured to the center of the upfield member of an aromatic doublet of multiplets and assigned to the ring protons (of the bidentate ligand L) meta to the ring nitrogens. [d] The methyl substituent of the Cp ring. [e] Cp ring protons. [f] Methylenic protons. [g] Olefinic protons.

Table III. ^{13}C NMR Spectroscopic Data[a]

compd	L ortho[b]	L meta[c]	L para[d]	L other	$-CH_3$[e]	Cp ring[f]		CO
$(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$					13.8	103.5	83.5, 82.9	226.40
BPA	150.6	124.7	150.6	36.1[g]				
$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]_2BPA$	158.9	125.2	150.8	36.1[g]	12.9	109.6	82.2, 80.9	236.18
BPY	151.1	121.8	145.6					
$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]_2BPY$	159.6	121.8	151.7		12.9	104.9	82.2, 81.9	*h*
BPE	151.1	121.9	144.4	131.3[i]				
$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]_2BPE$	159.2	122.0	151.2	144.3[i]	12.9	105.0	82.2, 81.6	*h*

[a] Chemical shifts in ppm relative to Me_4Si. Spectra were obtained in acetone-d_6. [b] Ring carbons ortho to ring nitrogens. [c] Ring carbons meta to ring nitrogens. [d] Quarternary ring carbons. [e] The methyl substituent of the Cp ring. [f] Carbons of the Cp ring, the quaternary carbon listed first. [g] Methylenic carbons. [h] Low signal to noise makes this assignment speculative. [i] Olefinic carbons.

$[CH_3C_5H_4Mn(CO)_2]_2N_2C_{12}H_{12}$: C, 59.58; H, 4.65; N, 4.96; mol wt, 564. Found: C, 60.46; H, 4.90; N, 5.86; mol wt, 563. Calcd for $[CH_3C_5H_4Mn(CO)_2]_2N_2C_{12}]H_{10}$: C, 59.79; H, 4.31; N, 4.98. Found: C, 59.87; H, 4.29; N, 5.14.

Attempts to use this synthetic procedure when L = pyrazine were unsuccessful.

Spectroscopic Methods. Electronic spectra were obtained under argon on a Cary 210 spectrophotometer. NMR spectra were obtained (Me_4Si reference) on a JEOL FX-90 Q spectrometer in degassed acetone-d_6 or in degassed deuterated THF. IR spectra were recorded in matched cells (loaded in a glovebag) on a Perkin-Elmer 283 spectrophotometer.

Results and Discussion

The reaction of the solvent adduct $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2\cdot THF$ with the bidentate ligands L proceeds cleanly at room temperature to give the dimeric derivatives $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]_2L$. We observed no tendency for the formation of monomeric compounds $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2L$, in contrast to the case for the pentacarbonyls of tungsten.[1] (When L = pyrazine, however, although color and infrared spectral changes indicated some substitution of the labile THF ligand, a binuclear product could not be isolated. With this smaller ligand, perhaps dimer formation is prevented for steric reasons.) The course of the dimer forming reaction can be monitored by changes in the IR spectrum of the reaction solution or by noting the change in color of the reaction solution from the burgundy of the THF adduct to that of the product: yellow (BPA), red (BPY), or purple (BPE). The colors of the products parallel the positions of the ligand-dependent metal-to-ligand charge-transfer absorptions (vide infra). Careful recrystallizations from THF/hexane give microcrystalline products that are stable only if handled carefully in the dark, under an inert atomsphere. The elemental analyses for these compounds are, we feel, quite acceptable given this extreme light and air sensitivity of the materials.

The infrared spectra in the carbonyl region of the compounds (Table I) exhibit two peaks of equal intensity, as expected, if one considers only the point symmetry at each metal center. The positions of these two peaks are relatively insensitive to the bridging ligand L but do change slightly in other solvents.

Table IV. Electronic Spectroscopic Data in Various Solvents[a]

compd	λ_{max}, nm acetone	THF	hexane
$(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$		328	
$(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2\cdot THF$		388 500	
$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]_2BPA$		380	410 500 sh
$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]_2BPY$	462	476	490 600 sh
$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]_2BPE$		480	525 650 sh
$(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2py$[b]			420 505 sh
$(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2\text{-}4\text{-}Acpy$[b]			535 650 sh

[a] Wavelengths of band maxima and shoulders (sh), in argon-protected solutions. [b] Taken from ref 6; in isooctane solution.

The title compounds have also been characterized by ^{1}H and ^{13}C NMR (Tables II and III, respectively). The peaks corresponding to the bridging ligands L are comparable in every way to those already reported[1] for the compounds $[W(CO)_5]_2L$. Here, however, coordination of the ligand L to the manganese metal centers does not generally result in deshielding of the pyridine rings, as was the case for tungsten.

Electronic spectroscopic data are reported in Table IV, along with the appropriate data previously reported[6] for the monomeric compounds $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2X$, where X = pyridine, 4-acetylpyridine. The electronic spectra for the dimeric compounds can be seen to be similar in all important ways to those of the monomeric derivatives, exhibiting very intense maxima and a shoulder to longer wavelengths in hexane. The compounds are photosensitive,[7] and molar ab-

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(7) We have found the dimers $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]_2L$ to be qualitatively much more photosensitive than the tungsten pentacarbonyls $[W(CO)_5]_2L$, and quantitative investigations of the photoreactivities of these two systems are under way.

sorptivities (ca. 10^3 M^{-1} cm^{-1} at peak maxima) were difficult to estimate. The spectra are sensitive both to the solvent and to the extent of conjugation in the bridging ligand L and are thus assigned to metal-to-ligand (d to π^*) charge-transfer transitions. Again, as previously found for the system $[W(CO)_5]_2L$,[1] the π^* levels in the bridging ligands L can be placed in the relative order BPA > BPY > BPE.

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Electronic Structure of Octachloroditungstate(II)

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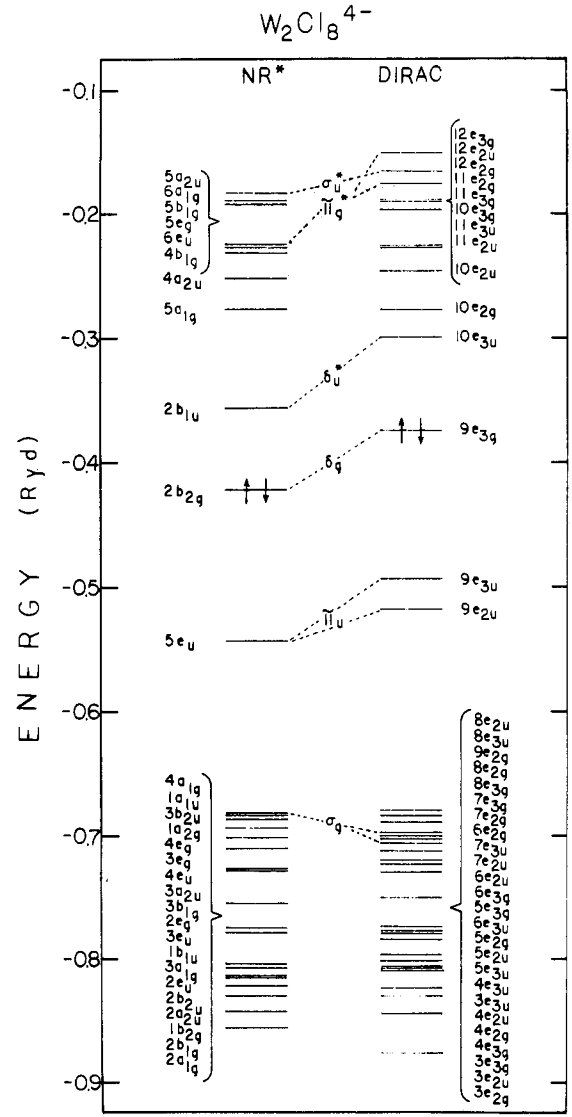
The existence of quadruple bonds between atoms of transition metals has been recognized for about 20 years.[1] These systems are characterized by having singlet ground states, short metal–metal bond lengths, and eclipsed conformations for the M_2X_8 species. In general, the excited states and photoelectron spectra of these systems are in good agreement with results of Xα–scattered-wave (SW) calculations.[2-4] A large number of such calculations have been made, and in recent years attention has been paid to possible relativistic effects in multiple bonds of the third transition series, by using quasi-relativistic calculations on complexes of tungsten and rhenium.[5,6] These calculations include the mass–velocity and Darwin corrections but omit the spin–orbit effect.[7,8] Here we report the first fully relativistic SW calculation on a molecule containing a multiple metal–metal bond, comparing relativistic and nonrelativistic results for $W_2Cl_8^{4-}$.

Our computational method incorporates the same approximations as conventional SW calculations but uses the Dirac equation rather than the Schroedinger wave equation as a starting point. Hence, all relativistic effects at the one-electron level are included. The development and applications of this method have recently been reviewed.[4,9] A D_{4h} geometry was assumed, with W–W and W–Cl bond lengths of 2.257 and 2.429 Å, respectively, and a W–W–Cl angle of 103.5°.[10] Our chlorine sphere radius (1.41 Å) is the same as that used in an earlier nonrelativistic calculation by Cotton and Kalbacher (CK);[11] the tungsten sphere radius (1.35 Å) is slightly larger than that used in the CK calculation since we assume a longer W–W bond (2.26 vs. 2.20 Å). Our nonrelativistic results were obtained from the Dirac program by setting the speed of light to a very large value (10^{15} au); except for the small change in geometry, however, they are identical with the CK results. A Watson sphere of charge 5+ and radius equal to that of the outer sphere (4.34 Å) was used to neutralize the charge of the cluster. Each iteration of the self-consistent calculation required about 5 min on a Burroughs B7800 computer; 38 iterations were required to converge the potential to a relative uncertainty of 8×10^{-5}.



(*) performed at $c \rightarrow \infty$

Figure 1. Nonrelativistic (NR) and relativistic (DIRAC) orbital energies for $W_2Cl_8^{4-}$.

Molecular orbital energies are shown in Figure 1. The principal relativistic shifts are similar to those seen in earlier quasi-relativistic studies:[5,6] the π_u, δ_g, and δ^*_u metal levels are shifted upward, while the metal σ_g bonding level is stabilized. The relative splittings among the upper three levels change only slightly (0.1–0.2 eV) upon incorporation of relativistic effects, whereas the relative distance between the σ_g and the upper levels increases by 0.8–0.9 eV. The predicted spin–orbit splitting of the π_u orbital is 0.33 eV, compared to a value of 0.4 eV seen in both $W_2Cl_4[P(CH_3)_3]_4$[5] and $W_2(mph)_4$.[12] These two compounds show a σ_g–π_u(j = $^1/_2$) splitting of 2.61 and 2.9 eV, respectively (calculated 2.44 eV), and splittings

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