Binucleating Coordination of *N*,*N*′-Ethylenebis(salicylideneamine) (H₂salen) to Low-Valent Group 6 Carbonyl Complexes

Donald J. Darensbourg* and Jennifer D. Draper

Department of Chemistry, Texas A&M University,
P.O. Box 30012, College Station, Texas 77842

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Figure 1. Schematic drawing of the salen ligand.

Introduction

While the coordination chemistry of *N*,*N*′-ethylenebis(sali-cylideneaminate) (salen; Figure 1) is well developed,[1] the organometallic chemistry of this ligand, with the exception of that of several Co and Ti complexes, has typically been neglected. This is surprising in that salen appears to be an extremely versatile and easily handled ligand. In addition, our research into the effects of π-donation on the coordination number of low-valent group 6 complexes of catechol, diami-nobenzene, and aminophenol,[2] to name a few, generated a curiosity as to what binding mode a ligand with more than two metal coordination sites would adopt when bound to a metal with labile carbonyl ligands. Because the binding mode of salen generally entails the coordination of four metal-binding sites to a single metal, (i.e., salen is normally a mononucleating ligand; Figure 2),[1] it was initially hoped that all four coordination sites would bind to one tungsten and produce a coordinatively unsaturated species stabilized by π-donation, similar in nature to those isolated in earlier studies from our laboratories.[2]

The aim of the present contribution is to demonstrate the preferred mode of binding of the salen ligand to a group 6 metal carbonyl. Herein we report the syntheses and solution and solid-state structures of [Et₄N]₂[M₂(CO)₈(salen)] complexes, where salen is behaving as a binucleating ligand, along with the qualitative rate of CO ligand exchange with free ¹³CO in these derivatives. To our knowledge, this is the first structurally characterized example of a zerovalent group 6 metal carbonyl complex incorporating the salen ligand.

Experimental Section

Methods and Materials. All manipulations were performed on a double-manifold Schlenk vacuum line under an atmosphere of argon or in an argon-filled glovebox. Solvents were dried and deoxygenated by distillation from the appropriate reagent under a nitrogen atmosphere. Photolysis experiments were performed using a mercury arc 450-W UV immersion lamp purchased from Ace Glass Co. Infrared spectra were recorded on a Mattson 6022 spectrometer with DTGS and MCT detectors. Routine infrared spectra were collected using a 0.10-mm CaF₂ cell. ¹³C NMR spectra were obtained on a Varian XL-200 spectrometer. ¹³CO was purchased from Cambridge Isotopes and used
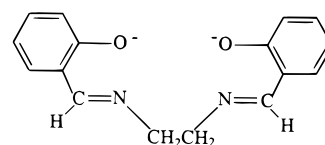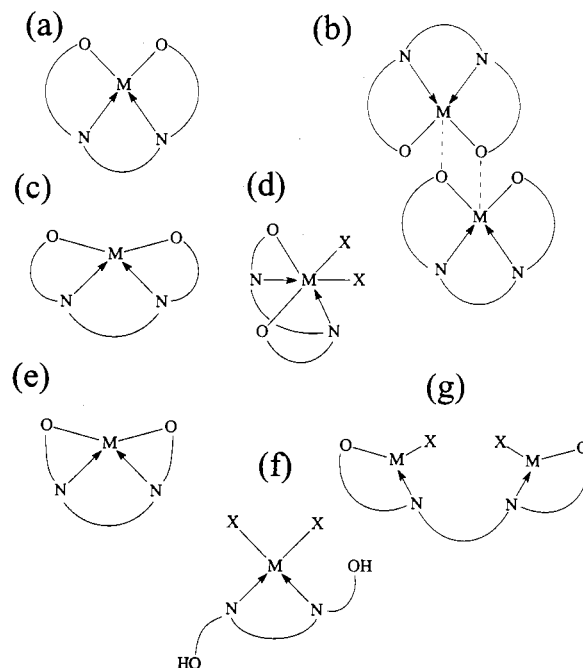

Figure 2. Coordination modes of salen: (a) planar coordination; (b) side coordination by the oxygen atom to the metal ion of an adjacent molecule; (c) planar structure of N₂O₂ with the umbrella shape of salicylideamine; (d) cis β-coordination; (e) mode with the metal ion located above the N₂O₂ plane; (f) bidentate coordination through nitrogens; (g) bridging between two metal centers.

as received. Cr(CO)₆ and W(CO)₆ were purchased from Strem Chemicals, Inc., and used without further purification. *N*,*N*′-ethyl-enebis(salicylideneamine) (H₂salen) was purchased from Aldrich Chemical Co. Microanalyses were performed by Canadian Microana-lytical Service, Ltd., Delta, BC, Canada.

Synthesis of the [Et₄N]₂[salen] Salt (salen = C₁₆H₁₄N₂O₂). The synthesis of this salt was accomplished by the slow addition of 2 equiv (2.8 mmol) of Et₄NOH, 25% in methanol, to a light yellow solution of H₂salen. While H₂salen is not entirely soluble in methanol, it is drawn into solution as the deprotonation occurs. The mixture was stirred for 60 min and the methanol was removed under vacuum overnight, yielding a dark yellow powder. Anal. Calcd for [Et₄N]₂[salen] (C₃₂H₅₄N₄O₂): C, 72.96; H, 10.33. Found: C, 72.25; H, 10.12. Alternatively, H₂salen was deprotonated using 2 equiv of NaOMe (0.076 g) and [PPN]Cl (0.82 g), dissolved in a solvent mixture of CH₃CN and MeOH, and added slowly to the MeOH solution of H₂salen. The yellow powder resulting from the removal of solvent was dissolved in CH₃CN, and the mixture was filtered through Celite to remove NaCl, yielding [PPN]₂[salen]. Anal. Calcd for [PPN]₂[salen] (C₈₈H₇₄N₄P₄-O₂): C, 78.67; H, 5.55. Found: C, 77.52; H, 5.41.

Synthesis of the [Et₄N]₂[M₂(CO)₈(salen)] and [PPN]₂[M₂(CO)₈-(salen)] Derivatives. The synthesis of the salts of [M₂(CO)₈(salen)]²⁻ [where M = Cr (**1**) or W (**2**) for the Et₄N⁺ derivative] was accomplished in yields in excess of 80% by the reaction of 2 equiv of M(CO)₅THF (prepared by the photolysis of 0.300 g of Cr(CO)₆ or 0.500 g of W(CO)₆ in THF) with 1 equiv (1.4 mmol) of doubly deprotonated salen in MeOH to yield a bright red solution. The solvents were removed from

(1) Aly, M. M. *Rev. Inorg. Chem.* **1996**, *16*, 315. (b) Aly, M. M. *Rev. Inorg. Chem.* **1996**, *16*, 329.
(2) Darensbourg, D. J.; Klausmeyer, K. K.; Mueller, B. C.; Reibenspies, J. H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1503. (b) Darensbourg, D. J.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1996**, *35*, 1529. (c) Darensbourg, D. J.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1996**, *35*, 1535.

Table 1. Crystallographic Data for Complex **2**

empirical formula	$W_2O_{10}N_4C_{40}H_{54}$	α, deg	106.907(7)
fw	1118.6	β, deg	90.904(10)
space group	$P\bar{1}$	γ, deg	93.654(12)
V, Å^3	2192.1(5)	T, K	193
Z	2	μ(Mo Kα), mm^{-1}	4.006
d_{calc}, g/cm^3	1.589	wavelength, Å	0.710 73
a, Å	8.432(2)	R,^{a} %	6.88
b, Å	14.769(2)	R_w,^{b} %	15.72
c, Å	18.448(2)		

^{a} $R = \sum|F_o - F_c|/\sum F_o$. ^{b} $R_w = \{[\sum w(F_o{}^2 - F_c{}^2)^2]/(\sum wF_o{}^2)\}^{1/2}$.

the reaction mixture under vacuum, and the resulting red solid was washed several times with hexanes to yield a red powder. Crystals were grown by the slow diffusion of diethyl ether into a concentrated acetonitrile solution of the complex at room temperature. Anal. Calcd for [Et$_4$N]$_2$[Cr$_2$(CO)$_8$(salen)] (**1**) (Cr$_2$O$_{10}$N$_4$C$_{40}$H$_{54}$): C, 56.21; H, 6.37. Found: C, 56.97; H, 6.17. Calcd for [Et$_4$N]$_2$[W$_2$(CO)$_8$(salen)] (**2**) (W$_2$O$_{10}$N$_4$C$_{40}$H$_{54}$): C, 42.95; H, 4.87. Found: C, 42.76; H, 4.77. Calcd for [PPN]$_2$[W$_2$(CO)$_8$(salen)] (**3**) (W$_2$P$_4$O$_{10}$N$_4$C$_{96}$H$_{74}$): C, 59.58; H, 3.85. Found: C, 60.00; H, 4.10.

X-ray Crystallography. [Et$_4$N]$_2$[W$_2$(CO)$_8$(salen)] (2). Crystal data and details of data collection are given in Table 1. A red block of **2** was mounted in a glass capillary with epoxy cement at room temperature. Preliminary examination and data collection were performed on a Nicolet R3m/v X-ray diffractometer (Mo Kα, $\lambda = 0.710$ 73 Å radiation). Cell parameters were calculated from the least-squares fitting of the setting angles for 24 reflections.

ω scans for several intense reflections indicated acceptable crystal quality. Data were collected for $4.0° \geq 2\theta \geq 50°$. Three control reflections, collected for every 97 reflections, showed no significant trends. Background measurements by stationary-crystal and stationary-counter techniques were taken at the beginning and end of each scan for half the total scan time. Lorentz and polarization corrections were applied to 7599 reflections, and a semiempirical absorption correction was applied. A total of 7587 unique reflections with $|I| \geq 2.0\sigma(I)$, were used in further calculations. All three structures were solved by direct methods [SHELXS program package, Sheldrick (1993)]. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded $R = 0.0688$, $R_w = 0.1572$, and $S = 1.094$ for **2**. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08. Neutral-atom scattering factors and anomalous scattering correction terms were taken from the *International Tables for X-ray Crystallography*.

Results

Synthesis and Spectral and Structural Characterization of [Et$_4$N]$_2$[M$_2$(CO)$_8$(salen)] (1, 2). The synthesis of [Et$_4$N]$_2$-[M$_2$(CO)$_8$(salen)] (**1**, **2**) is accomplished in greater than 80% yield by the labile ligand displacement reaction of M(CO)$_5$THF (obtained via photolysis of Cr(CO)$_6$ or W(CO)$_6$ in THF solution) and the doubly deprotonated tetraethylammonium or PPN salt of H$_2$salen. The reaction proceeds by way of the displacement of THF by the phenolic oxygen and/or nitrogen atom, quickly followed by chelation to the metal center with concomitant loss of CO. As evidenced by X-ray crystallography (vide infra), the salen ligand twists about the C−C bond in the ethylene bridge between the two nitrogen atoms, allowing the phenolic oxygen and nitrogen on the opposite side of the ligand to chelate to a second M(CO)$_5$THF adduct, similarly displacing a THF followed by loss of CO. This configuration was adopted even when the stoichiometry (1:1 tungsten to salen) of the reaction mixture did not favor the formation of such a complex. The stoichiometry was later adapted to optimize the yield of

Table 2. Stretching Frequencies of the Carbonyl Ligands in the M$_2$(CO)$_8$(salen)$^{2-}$ (**1**, **2**) Anions

complex^a	ν(CO), cm^{-1}			
Cr$_2$(CO)$_8$(salen)$^{2-}$	1994.3 (w)	1872.7 (vs)	1849 (sh)	1787.9 (m)^b
W$_2$(CO)$_8$(salen)$^{2-}$	1990.4 (w)	1859.3 (vs)	1841 (sh)	1784.1 (m)^b

^{a} As the tetraethylammonium salt. ^{b} Spectra determined in CH$_3$CN.
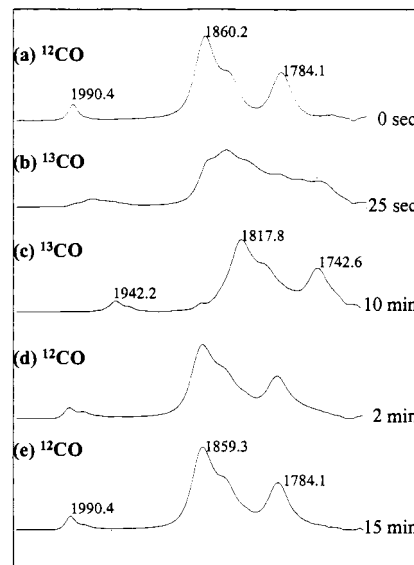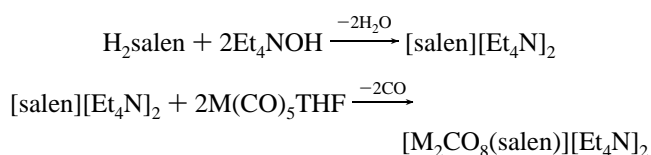

Figure 3. Infrared spectra of **2,** as a function of time, at ambient temperature: (a) under ^{12}CO, before experiment; (b) under ^{13}CO, 25 s; (c) under ^{13}CO, 10 min; (d) under ^{12}CO, 2 min; (e) under ^{12}CO, 15 min.

this complex. Scheme 1 summarizes the synthesis of these complexes.

Scheme 1

$$H_2salen + 2Et_4NOH \xrightarrow{-2H_2O} [salen][Et_4N]_2$$

$$[salen][Et_4N]_2 + 2M(CO)_5THF \xrightarrow{-2CO}$$
$$[M_2CO_8(salen)][Et_4N]_2$$

Complexes **1** and **2** exhibit a four-band pattern in the carbonyl region of their infrared spectra consistent with a cis-disubstituted tetracarbonyl complex. These frequencies are provided in Table 2. The complete enrichment of complex **2** with ^{13}C-labeled CO was accomplished in approximately 10 min by the addition of an atmosphere of ^{13}CO to an acetonitrile solution of **2** at ambient temperature, indicative of very labile CO ligands. Complex **2** quantitatively returned to the unenriched species upon the addition of an atmosphere of purified ^{12}CO (Figure 3). A conservative estimate of $t_{1/2}$ for the rate of CO exchange at ambient temperature is approximately 1 min, leading to a calculated rate constant of 1.2×10^{-2} s^{-1}. This may be compared with the value of k for dissociation of CO in the W(CO)$_5$OPh$^-$ anion where k was determined to be 2.15×10^{-2} s^{-1} at 5 °C.[3]

Table 3 lists the ^{13}C NMR data for the complex in the carbonyl region of the spectra for complexes **1** and **2**. Chemical shift data for the M(CO)$_4$ moieties reveal a slight electronic difference between the CO ligand trans to oxygen and the CO

(3) Darensbourg, D. J.; Klausmeyer, K. K.; Draper, J. D.; Chojnacki, J. A.; Reibenspies, J. H. *Inorg. Chim. Acta* **1998**, *270*, 405.

Table 3. ^{13}C NMR Data for the Carbonyl Ligands in $M_2(CO)_8(salen)^{2-}$ (**1**, **2**)

complex	^{13}C resonance, ppm		
	CO (axial)	CO (trans to N)	CO (trans to O)
$Cr_2(CO)_8(salen)^{2-}$ ^{a,b}	216.5	232.4	232.5
$W_2(CO)_8(salen)^{2-}$ ^{a,b}	208.5	215.9	217.3

^{a} Spectra determined in acetonitrile-d_3. ^{b} As the tetraethylammonium salt.
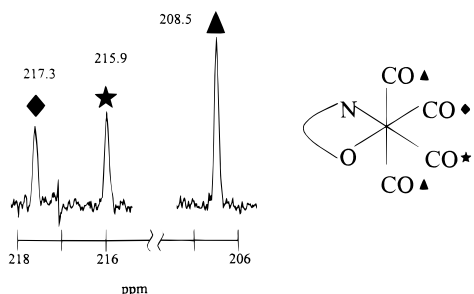
Figure 4. ^{13}C NMR spectrum of **2** with the labeling scheme.
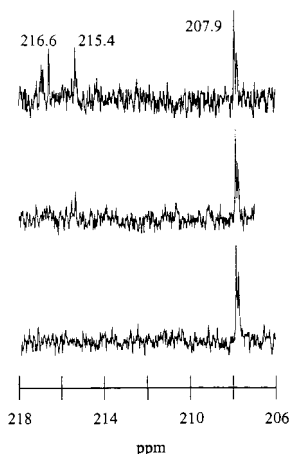
Figure 5. Low-temperature ^{13}C NMR spectrum of **2** illustrating stereoselectivie CO exchange.

ligand trans to nitrogen. The ^{13}C NMR spectra of complexes **1** and **2** display three signals for the carbonyl carbons in an approximate 2:1:1 intensity ratio (Figure 4). The more intense resonance for the two carbonyl ligands cis to both the nitrogen and oxygen atoms of the salen ligand is observed upfield from the two smaller signals assigned to the carbonyl ligands trans to the oxygen and nitrogen donors. The assignment of the δ-(^{13}C) carbonyl resonance trans to nitrogen upfield of the signal due to the carbonyl trans to oxygen is consistent with previous assignments.[4,5] When an atmosphere of ^{13}CO is added to an NMR tube of **2** in CD_3CN maintained at -20 °C and the NMR spectrum is monitored (Figure 5), the first ^{13}C resonance to appear corresponds to the axial carbonyl ligands cis to both the nitrogen and oxygen atoms (208 ppm). The ^{13}C signal due to the carbonyl ligand trans to the nitrogen (and yet cis to oxygen) appears next (215 ppm), followed by the lowest field signal (217 ppm). At the end of the experiment, after the sample is allowed to equilibrate all CO groups, the ^{13}C NMR spectrum is identical to that normally observed for a randomly ^{13}C-enriched or natural abundance ^{13}C CD_3CN solution of **2**. The function

(4) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1. (b) Darensbourg, D. J.; Wiegreffe, H. P. *Inorg. Chem.* **1990**, *29*, 592.
(5) Darensbourg, D. J.; Atnip, E. V.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1994**, *33*, 5230. (b) Darensbourg, D. J.; Draper, J. D.; Reibenspies, J. H. *Inorg. Chem.* **1997**, *36*, 3648.

Table 4. Bond Lengths (Å) and Angles (deg) for **2**^{a}

W(1)−C(1)	2.06(2)	O(12)−C(2)	1.15(2)
W(1)−C(2)	1.91(2)	N(1)−C(11)	1.28(2)
W(1)−C(3)	1.920(14)	N(1)−C(12)	1.55(2)
W(1)−C(4)	1.98(3)	C(5)−C(6)	1.40(2)
W(1)−O(5)	2.158(9)	C(5)−C(10)	1.44(2)
W(1)−N(1)	2.220(13)	C(6)−C(7)	1.33(2)
O(1)−C(1)	1.13(2)	C(7)−C(8)	1.39(2)
O(2)−C(2)	1.19(2)	C(8)−C(9)	1.37(2)
O(3)−C(3)	1.19(2)	C(9)−C(10)	1.41(2)
O(4)−C(4)	1.22(3)	C(10)−C(11)	1.43(2)
O(5)−C(5)	1.30(2)	C(12)−C(12)#1	1.44(3)
C(2)−W(1)−C(3)	86.3(6)	C(11)−N(1)−C(12)	114.1(13)
C(2)−W(1)−C(4)	89.5(8)	C(11)−N(1)−W(1)	128.7(11)
C(3)−W(1)−C(4)	82.4(6)	C(12)−N(1)−W(1)	117.2(9)
C(2)−W(1)−C(1)	86.0(8)	O(1)−C(1)−W(1)	170(2)
C(3)−W(1)−C(1)	85.1(7)	O(2)−C(2)−W(1)	177(2)
C(4)−W(1)−C(1)	166.9(7)	O(3)−C(3)−W(1)	178.7(13)
C(2)−W(1)−O(5)	94.7(5)	O(4)−C(4)−W(1)	170.9(13)
C(3)−W(1)−O(5)	178.9(5)	O(5)−C(5)−C(6)	120.9(13)
C(4)−W(1)−O(5)	97.8(5)	O(5)−C(5)−C(10)	124.4(12)
C(1)−W(1)−O(5)	94.8(6)	C(6)−C(5)−C(10)	114.4(12)
C(2)−W(1)−N(1)	176.3(6)	C(7)−C(6)−C(5)	126(2)
C(3)−W(1)−N(1)	96.6(5)	C(6)−C(7)−C(8)	119.0(14)
C(4)−W(1)−N(1)	93.2(6)	C(9)−C(8)−C(7)	120(2)
C(1)−W(1)−N(1)	91.9(7)	C(8)−C(9)−C(10)	121(2)
O(5)−W(1)−N(1)	82.3(4)	C(9)−C(10)−C(11)	117.0(14)
C(5)−O(5)−W(1)	133.0(9)	C(9)−C(10)−C(5)	119.7(13)
C(11)−C(10)−C(5)	123.2(12)	C(12)#1−C(12)−N(1)	107(2)
N(1)−C(11)−C(10)	128(2)		

^{a} Estimated standard deviations are given in parentheses.
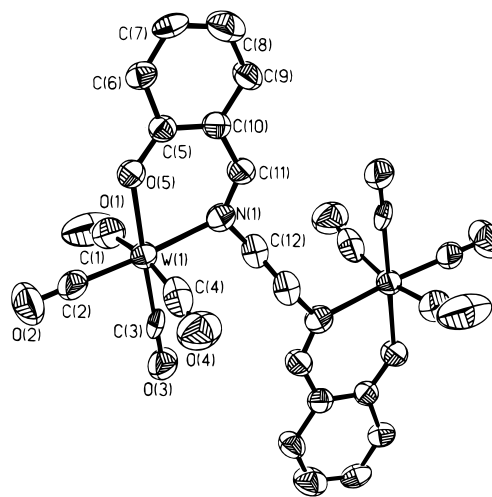
Figure 6. Thermal ellipsoid drawing of the anion of **2** with atomic numbering scheme.

of the phenoxide group oxygen as a cis-labilizing ligand is aptly illustrated by this experiment.

Crystals of **2** $[Et_4N]_2[W_2(CO)_8(salen)]$ were grown from the slow diffusion of ether into a concentrated CH_3CN solution of the appropriate complex over several days. Maroon blocks in the space group $P\bar{1}$ were obtained for **2**. Two independent anions and four cations were observed in the unit cell of **2**; similar bond distances and angles are seen in the two independent anions. Table 4 lists selected bond lengths and angles, while Figure 6 shows a thermal ellipsoid drawing of the anion of **2**.

The structure of complex **2** consists of a doubly deprotonated salen ligand that forms a chelate ring to each of two tetracarbonylmetal centers through a nitrogen and an oxygen atom, forming a distorted octahedron at each metal center. The W−N bond length was determined to be 2.22(1) Å, slightly shorter

than that found in $W(CO)_5$(piperidine), 2.331(5) Å,[6] and similar to the W−N bond length of 2.26(1) Å in $W(CO)_5$(pyridine).[7] The W−O bond length of 2.16(1) Å in **2** is nearly identical to the W−O bond length of 2.19(2) Å observed in the $W(CO)_5OPh^-$ anion.[8] The salen ligand forms an 82.3(4)° bite angle with the metal atom. The average W−C_{ax} bonds at 2.02(3) Å are longer than the average W−C_{eq} bonds determined to be 1.92(2) Å; there is no significant difference, however, between the W−C bonds for CO groups alternately trans to nitrogen or oxygen (1.91(2) and 1.92(1) Å, respectively).

Conclusions

Herein we have described the synthesis, ^{13}C NMR and *ν*-(CO) infrared spectroscopies, and X-ray structure of a novel tungsten carbonyl complex of salen. While a coordinatively unsaturated derivative was not observed, ^{13}CO exchange studies reveal that the carbonyl ligands on these complexes are nevertheless very labile, similar to those in phenoxide derivatives of $W(CO)_6$. Infrared experiments that monitor the formation of the enriched species show that CO exchange occurs rapidly and reversibly at ambient temperature. Low-temperature NMR experiments indicate that this complex undergoes stereoselective CO exchange. The axial carbonyls, cis to both oxygen and nitrogen, have the fastest rate of exchange, followed by the equatorial CO ligand trans to nitrogen (yet still cis to oxygen) and last the carbonyl trans to oxygen. Hence, the anionic oxygen donor group in salen is demonstrated to be cis labilizing.[9] The X-ray crystal structure obtained from crystals of the tungsten complex reveal that salen twists about the carbon−carbon bond in the ethylene bridge, connecting the two nitrogens to allow for the coordination of two metal centers. Interestingly, this bimetallic bonding mode occurred even when the stoichiometry of the reaction mixture did not favor its formation. Finally, while this binucleating coordination mode is not common, it is not without precedence; several examples similar to the one presented here are given in the literature for salen[10] or its analogues.[11] This is, however, the first report of a crystal structure of a zerovalent metal carbonyl complex incorporating salen.

Supporting Information Available: X-ray crystallographic files, in CIF format, for complex **1** are available on the Internet only. Access information is given on any current masthead page.

(6) Moralejo, C.; Langford, C. H.; Bird, P. H. *Can. J. Chem.* **1991**, *69*, 2033.

(7) Klement, U. *Z. Kristallogr.* **1993**, *208*, 111. (b) Tutt, L.; Zink, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 5830.

(8) Darensbourg, D. J.; Mueller, B. L.; Bischoff, C. J.; Chojnacki, S. S. *Inorg. Chem.* **1991**, *30*, 2418.

(9) (a) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366. (b) Davy, R. D.; Hall, M. B. *Inorg. Chem.* **1989**, *28*, 3524.

(10) Calligaris, M.; Nardin, G.; Randaccia, L. *J. Chem. Soc. D* **1970**, 1079. (b) Gatehouse, B. M.; Reichert, B. E.; West, B. O. *Acta Crystallogr., Sect. B* **1974**, *30*, 2451. (c) Bombieri, G.; Gilli, G.; Hernandez-Cano, F.; Mazzi, U. *Izv. Jug. Cent. Kristallogr., Ser. A* **1976**, *11*, 56. (d) Lahuerta, P.; LaTorre, J.; Martinez-Manez, R.; Garcia-Granda, S.; Gomez-Beltran, F. *Inorg. Chim. Acta* **1990**, *168*, 149. (e) Herrmann, W. A.; Rauch, M. U.; Artus, G. R. J. *Inorg. Chem.* **1996**, *35*, 1988.

(11) Solari, E.; Latronico, M.; Blech, P.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1996**, *35*, 4526.