Inorg. Chem. 1984, 23, 1807–1810

Contribution from the Departments of Chemistry and Physics and Astronomy,
Vanderbilt University, Nashville, Tennessee 37235

Reactions of Coordinated Molecules. 36. Crystal and Molecular Structure of a Rhenaacetylacetonate Anion as the Benzamidinium Salt

P. GALEN LENHERT,[1a] C. M. LUKEHART,*[1b] PETER D. SOTIROPOULOS,[1b] and K. SRINIVASAN[1b]

Received June 7, 1983

The rhenaacetylacetone molecule $[cis\text{-}(OC)_4Re(CH_3CO)_2]H$ reacts with benzamidine to give the benzamidinium salt of the corresponding rhenaacetylacetonate anion, $[PhC(NH_2)_2][cis\text{-}(OC)_4Re(CH_3CO)_2]$. This salt crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.037$ (2) Å, $b = 13.155$ (2) Å, $c = 8.004$ (2) Å, $\alpha = 106.74$ (2)°, $\beta = 103.16$ (2)°, $\gamma = 89.91$ (2)°, $V = 885.2$ Å^3, and $Z = 2$. The benzamidinium cation affords a very stable salt of this organometallic anion. A chain network of O···H–N hydrogen bonds is present throughout the lattice. The structural characterization of this diacetylrhenate complex provides structural data for a basic type of metalla β-diketonate complex.

Introduction

The rhenaacetylacetone molecule **1** reacts with benzamidine free base at room temperature to give the benzamidinium salt of the corresponding rhenaacetylacetonate anion, **2**.

$$\underset{\mathbf{1}}{[cis\text{-}(OC)_4Re(CH_3CO)_2]H} + PhC(NH)NH_2 \rightarrow \underset{\mathbf{2}}{[PhC(NH_2)_2][cis\text{-}(OC)_4Re(CH_3CO)_2]}$$

Under these conditions, a simple acid–base reaction occurs rather than a Schiff-base condensation, which is a well-known type of reaction for rhena β-diketones.[2–5] The salt **2** crystallizes readily as large yellow platelike crystals that are quite stable to heat and to exposure to air. The molecular structure of **2** was undertaken to unambiguously characterize a rhenaacetylacetonate anion. The organometallic complex represents the "free-ligand" form of one of the basic classes of metalla β-diketonate molecules.[6] Structural data for this anionic complex are needed to permit a nearly complete comparative summary of structural data for a variety of metalla β-diketonate complexes and their derivatives. These complexes usually contain an acyl ligand that is O bonded to a Lewis acid. The structure of such μ-η^2-acyl ligands is relevant to the chemistry of Lewis acid adducts of acyl ligands[7] and to the characterization of dinuclear organometallic complexes that contain bridging ligands of this type.[8]

The structure of the unsymmetrical mangana β-diketonate complex $[Me_4N][cis\text{-}(OC)_4Mn(PhCO)(CH_3CO)]$[9] has been reported previously.

Experimental Section

The general reaction conditions, solvent purification, and spectrometer designations used are specified elsewhere.[5] Microanalysis was performed by Galbraith Laboratories, Inc., Knoxville, TN. Benzamidine free base was prepared by treating benzamidine hydrochloride with KOH in a minimum volume of water. The free base was isolated by extraction into methylene chloride. The extraction solution was dried over $MgSO_4$.

Table I. Summary of X-ray Crystallographic Data for Complex **2**

lattice consts: $a = 9.037$ (2) Å, $b = 13.155$ (3) Å, $c = 8.004$ (2) Å, $\alpha = 106.74$ (2)°, $\beta = 103.16$ (2)°, $\gamma = 89.91$ (2)°
radiation: λ(Mo Kα_1) = 0.709 26 Å (cell consts), λ(Mo Kα) = 0.710 10 Å (data colln)
temp: 20 °C
filters: 4-foil Nb for $2\theta = 0$–11°; 2-foil Nb for $2\theta = 11$–60°
cryst dimens: 0.75 × 0.75 × 0.25 mm
abs coeff: $\mu = 69.85$ cm^{-1}
transmissn factors: range = 0.1886–0.0250; av = 0.1280
abs cor: ORABS numerical integration; 8 × 8 × 8 Gaussian grid
diffractometer: four-circle, computer-controlled Picker with Picker FACS-1 control software
scan technique: 2θ, step-scan, 13 steps/reflcn
range in 2θ: 1–60°
octants collcd: $\pm h, \pm k, \pm l$
no. of reflcns collcd: 10 871 (5174 indep)
intens loss: 11% over 152 h of exposure
soln: sharpened, origin-removed Patterson map; successive difference maps
hydrogen atoms: all located on maps and all but 2 refined
final R factors: $R = 4.8\%$; $R_w = \{[\Sigma w(|F_o| - |F_c|)^2]/\Sigma w|F_o|^2\}^{1/2} = 5.3\%$

Preparation of 2. To a solution of 0.20 g (0.52 mmol) of **1** in 40 mL of methylene chloride was added 0.062 g (0.52 mmol) of benzamidine free base at 25 °C. A white precipitate formed within the first 30 s, and the reaction solution was stirred for a total of 2 h. After this time, isolation of the white precipitate afforded 0.144 g (55%) of crude **2**, which was crystallized from ether solution at −15 °C as yellow platelike crystals: mp 122–124 °C; IR (CH_2Cl_2) ν(CO) 2065 (w), 1990 (m, sh), 1950 (vs), 1923 (s), ν(acyl) 1580 (w) cm^{-1}; ^1H NMR (acetone-d_6) δ 2.37 (s, 6, 2 CH_3), 7.35, 7.44, 7.52, 7.58, 7.75, 7.84 (m, 5, Ph), NH protons appearing as a very broad peak at δ 3.27 when observed. Anal. ($C_{15}H_{15}N_2O_6Re$) C, H, N.

Crystal and Molecular Structure of 2. A summary of the principal X-ray crystallographic data is provided in Table I. A crystal was mounted in a glass capillary, and a series of precession photographs indicated only $\bar{1}$ symmetry. A Delauney reduction was used to obtain a reduced triclinic cell. Data collection software for the Picker FACS-I system[10] and the ORABS program[11] used for absorption corrections have been reported previously. Atomic scattering factors for neutral atoms were those tabulated by Cromer and Mann,[12] and the anomalous scattering factors were those given by Cromer and Liberman.[13] The average and maximum shift-to-error ratios for the final refinement cycle were 0.02 and 0.14. A final difference synthesis revealed four relatively large residual regions of electron density within 1.0 Å from Re. These peak densities were 4.2, 3.0, −2.1, and −2.8 e Å^{-3}; outside

---

(1) (a) Department of Physics and Astronomy. (b) Department of Chemistry.
(2) Lukehart, C. M.; Zeile, J. V. *J. Am. Chem. Soc.* **1978**, *100*, 2774–2778.
(3) Lukehart, C. M.; Zeile, J. V. *Inorg. Chem.* **1978**, *17*, 2369–2374.
(4) Baskar, A. J.; Lukehart, C. M.; Srinivasan, K. *J. Am. Chem. Soc.* **1981**, *103*, 1467–1472.
(5) Lukehart, C. M.; Raja, M. *Inorg. Chem.* **1982**, *21*, 1278–1280.
(6) Lukehart, C. M. *Acc. Chem. Res.* **1981**, *14*, 109–116.
(7) Stinson, R. E.; Shriver, D. F. *Inorg. Chem.* **1980**, *19*, 1141–1145.
(8) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360–6368.
(9) Casey, C. P.; Bunnell, C. A. *J. Chem. Soc., Chem. Commun.* **1974**, 733.
(10) Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *8*, 568–570.
(11) Wehe, D. J.; Busing, W. R.; Lenz, H. A. "ORABS, A Fortran Program for Calculating Single-Crystal Absorption Corrections", Report ORNL-TM-229; Oak Ridge National Laboratory: Oak Ridge, TN, 1962.
(12) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321–324.
(13) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.

0020-1669/84/1323-1807$01.50/0

Table II. Final Positional Parameters[a] for $[PhC(NH_2)_2][cis\text{-}(OC)_4Re(CH_3CO)_2]$ (2)

atom[b]	*x*	*y*	*z*
Re	0.04162 (2)	0.20237 (2)	0.32814 (3)
O(1)	0.0665 (9)	0.1162 (6)	−0.0677 (9)
O(2)	−0.2873 (6)	0.1009 (5)	0.2480 (11)
O(3)	0.1736 (8)	0.0092 (5)	0.4481 (10)
O(4)	0.0533 (8)	0.3363 (6)	0.7214 (8)
O(5)	−0.0038 (5)	0.3754 (4)	0.1382 (7)
O(6)	0.2992 (5)	0.3746 (4)	0.4368 (7)
C(1)	0.0542 (8)	0.1435 (5)	0.0770 (10)
C(2)	−0.1665 (7)	0.1375 (5)	0.2795 (10)
C(3)	0.1251 (8)	0.0792 (6)	0.4013 (10)
C(4)	0.0467 (7)	0.2844 (6)	0.5782 (9)
C(5)	−0.0492 (6)	0.3390 (5)	0.2464 (8)
C(6)	0.2695 (6)	0.2772 (5)	0.3797 (8)
C(7)	−0.1816 (10)	0.3934 (7)	0.3121 (13)
C(8)	0.4012 (8)	0.2115 (8)	0.3454 (13)
N(1)	−0.4232 (7)	0.4759 (5)	0.6948 (8)
N(2)	−0.1966 (6)	0.4675 (5)	0.8893 (9)
C(10)	−0.3363 (6)	0.4301 (4)	0.8014 (7)
C(11)	−0.4002 (6)	0.3325 (5)	0.8251 (7)
C(12)	−0.5469 (7)	0.3306 (6)	0.8495 (9)
C(13)	−0.6066 (9)	0.2391 (9)	0.8703 (14)
C(14)	−0.5244 (12)	0.1511 (8)	0.8614 (16)
C(15)	−0.3780 (11)	0.1543 (6)	0.8385 (13)
C(16)	−0.3145 (9)	0.2455 (5)	0.8217 (11)
H(71)	−0.267	0.340	0.290
H(72)	−0.136 (11)	0.442 (8)	0.430 (14)
H(73)	−0.238 (9)	0.438 (6)	0.223 (10)
H(81)	0.425	0.167	0.432
H(82)	0.375 (10)	0.157 (7)	0.243 (12)
H(83)	0.477 (11)	0.248 (8)	0.342 (12)
H(1)	−0.513 (12)	0.431 (9)	0.594 (15)
H(2)	−0.396 (13)	0.537 (9)	0.683 (15)
H(3)	−0.139 (6)	0.414 (5)	0.945 (8)
H(4)	−0.144 (8)	0.526 (6)	0.876 (10)
H(12)	−0.610 (7)	0.399 (5)	0.841 (8)
H(13)	−0.718 (10)	0.244 (7)	0.890 (11)
H(14)	−0.574 (9)	0.097 (7)	0.913 (10)
H(15)	−0.316 (13)	0.099 (10)	0.816 (15)
H(16)	−0.211 (10)	0.248 (7)	0.824 (11)

[a] *x*, *y*, and *z* are fractional coordinates with estimated standard deviations in parentheses. Atoms H(71) and H(81) were not refined. [b] Hydrogen atom designations involving two digits refer to the hydrogen atom that is bonded to the carbon atom designated by the first digit or by both digits. H(1) and H(2) and H(3) and H(4) are bonded to N(1) and N(2), respectively.

this region the maximum and minimum values were 0.56 and −0.56 e Å^{-3}. All hydrogen atoms were located on difference electron density maps, and all hydrogen atoms except H(71) and H(81) refined properly. A complete listing of final positional parameters is provided in Table II. The values were used before rounding to calculate the final structure factors. A complete listing of final positional and thermal parameters and a listing of F_o and F_c values are included in the supplementary material.

Structure factor, electron density, and bond distance and angle calculations were performed with the X-RAY 67 programs[14] as implemented and updated on the Vanderbilt DEC-10 computer.

Results

An ORTEP view of **2** showing the atomic numbering scheme is shown in Figure 1. Final atomic positional parameters are provided in Table II. Selected interatomic distances and angles are presented in Table III.

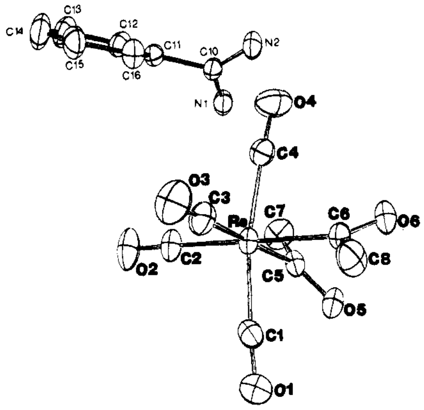


Figure 1. ORTEP view of the asymmetric unit of $[PhC(NH_2)_2][cis\text{-}(OC)_4Re(CH_3CO)_2]$ (**2**), showing the atomic numbering scheme (thermal ellipsoids at 30% probability). Hydrogen atoms are not shown for clarity.

Table III. Selected Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations for $[PhC(NH_2)_2][cis\text{-}(OC)_4Re(CH_3CO)_2]$ (**2**)

Interatomic Distances			
Re–C(1)	1.965 (7)	C(11)–C(12)	1.385 (9)
Re–C(2)	1.974 (6)	C(11)–C(16)	1.377 (9)
Re–C(3)	1.969 (8)	C(12)–C(13)	1.39 (2)
Re–C(4)	1.971 (7)	C(13)–C(14)	1.37 (2)
Re–C(5)	2.181 (6)	C(14)–C(15)	1.38 (2)
Re–C(6)	2.183 (6)	C(15)–C(16)	1.39 (2)
C(1)–O(1)	1.14 (1)	N(1)–H(1)	1.04 (10)
C(2)–O(2)	1.138 (8)	N(1)–H(2)	0.9 (2)
C(3)–O(3)	1.14 (2)	N(2)–H(3)	1.02 (7)
C(4)–O(4)	1.141 (9)	N(2)–H(4)	0.95 (9)
C(5)–O(5)	1.24 (1)	C(12)–H(12)	1.07 (7)
C(6)–O(6)	1.237 (7)	C(13)–H(13)	1.06 (10)
C(5)–C(7)	1.51 (2)	C(14)–H(14)	1.06 (10)
C(6)–C(8)	1.50 (1)	C(15)–H(15)	0.9 (2)
C(10)–N(1)	1.301 (9)	C(16)–H(16)	0.94 (9)
C(10)–N(2)	1.314 (7)	H(1)–O(6)	1.87 (10)
C(10)–C(11)	1.488 (9)	H(3)–O(5)	1.93 (7)

Interatomic Angles			
C(1)–Re–C(4)	169.9 (4)	Re–C(6)–C(8)	121.0 (5)
C(2)–Re–C(6)	178.7 (3)	O(5)–C(5)–C(7)	114.6 (7)
C(3)–Re–C(5)	179.6 (3)	O(6)–C(6)–C(8)	115.6 (6)
C(1)–Re–C(2)	93.0 (4)	N(1)–C(10)–N(2)	122.8 (7)
C(1)–Re–C(3)	94.7 (4)	N(1)–C(10)–C(11)	117.9 (5)
C(1)–Re–C(5)	85.1 (3)	N(2)–C(10)–C(11)	119.3 (6)
C(1)–Re–C(6)	86.9 (3)	C(10)–C(11)–C(12)	118.9 (6)
C(2)–Re–C(3)	89.7 (3)	C(10)–C(11)–C(16)	120.3 (6)
C(2)–Re–C(4)	94.6 (3)	C(12)–C(11)–C(16)	120.9 (7)
C(2)–Re–C(5)	90.7 (3)	C(11)–C(12)–C(13)	118.7 (8)
C(3)–Re–C(4)	92.0 (4)	C(12)–C(13)–C(14)	120.9 (9)
C(3)–Re–C(6)	91.6 (3)	C(13)–C(14)–C(15)	120 (2)
C(4)–Re–C(5)	88.2 (3)	C(14)–C(15)–C(16)	120.4 (9)
C(4)–Re–C(6)	85.4 (3)	C(15)–C(16)–C(11)	119.2 (8)
C(5)–Re–C(6)	88.0 (3)	H(1)–N(1)–C(10)	123 (7)
Re–C(1)–O(1)	175.1 (7)	H(1)–N(1)–H(2)	116 (10)
Re–C(2)–O(2)	178.4 (9)	H(2)–N(1)–C(10)	119 (7)
Re–C(3)–O(3)	178.3 (7)	H(3)–N(2)–C(10)	112 (4)
Re–C(4)–O(4)	176.3 (8)	H(3)–N(2)–H(4)	121 (6)
Re–C(5)–O(5)	124.3 (5)	H(4)–N(2)–C(10)	125 (5)
Re–C(5)–C(7)	121.1 (6)	O(5)–H(3)–N(2)	153 (4)
Re–C(6)–O(6)	123.4 (5)	O(6)–H(1)–N(1)	167 (10)

The structure of the $(OC)_4Re$ moiety is as expected for a *cis*-$L_2Re(CO)_4$ complex. The average values of the Re–C and C–O distances and the Re–C–O angles for the four terminal CO ligands are 1.970 (7) Å, 1.14 (1) Å, and 177.0 (8)°, respectively. The angles defining the principal coordination axes about the Re atom are C(1)–Re–C(4) = 169.9 (4)°, C(2)–Re–C(6) = 178.7 (3)°, and C(3)–Re–C(5) = 179.6 (3)°. The C(1)–Re–C(4) angle is significantly different from 180°. The single represents a tilting of the two axial CO ligands toward the rhenaacetylacetone portion of the molecule. This tilting is consistent with the $(OC)_4Re$ moiety acting as a metalla analogue to an sp^2 methine group.[15] The average

---

(14) Stewart, J. M. "X-ray 67 Program System for X-ray Crystallography for the Univac 1108, CDC 3600/6600, IBM 360/50, 65, 75, IBM 7094", Technical Report Tr-67-58; Computer Science Center, University of Maryland: College Park, MD, 1967.

(15) Lukehart, C. M.; Srinivasan, K. *Organometallics* **1982**, *1*, 1247–1249.

Table IV. Re–C and C–O Distances for Acetyl Ligands in Rhena β-Diketonate Complexes and Related Molecules

complex	Re–C(acetyl) dist, Å	C(acetyl)–O dist, Å	ref
cis-$(OC)_4Re(NPhH_2)[C(O)CH_3]$ (6)	2.211 (6)	1.214 (7)	20
cis-$(OC)_4Re[C(=NPhH)(CH_3)][C(O)CH_3]$ (7)	2.22 (2)	1.19 (2)	2
cis-$(OC)_4Re[C(=NRH)(CH_3)][C(O)CH_3]^a$ (8)	2.21 (2)	1.21 (2)	4
cis-$(OC)_4Re(CH_3CO)_2^-$ (9)	2.183 (6)	1.237 (7)	this work
	2.181 (6)	1.24 (1)	this work
[*cis*-$(OC)_4Re(CH_3CO)_2]H^b$ (10)	2.18 (2)	1.29 (2)	16
	2.15 (2)	1.25 (2)	
[*cis*-$(OC)_4Re(CH_3CO)_2]H^c$ (10)	2.18 (2)	1.25 (2)	17
	2.13 (2)	1.28 (2)	
[*cis*-$(OC)_4Re(CH_3CO)_2]_2Cu$ (11)	2.155 (4)	1.249 (5)	21
	2.149 (5)	1.241 (6)	
[*fac*-$(OC)_3Re(CH_3CO)_3]BCl$ (12)	2.10 (3)	1.31 (3)	22, 23
	1.93 (2)	1.42 (3)	
[*fac*-$(OC)_3Re(CH_3CO)_3]BBr$ (13)	2.06 (2)	1.31 (3)	23
	2.03 (3)	1.39 (2)	

[a] R is L-$C(CH_3)(H)CO_2Et$. [b] X-ray structure determination. [c] Neutron structure determination.

value of the C–Re–C angles between adjacent ligands is 90.0 (3)°.

The two acetyl ligands are rotated relative to one another such that the non-hydrogen atoms are not coplanar. The O(5)···O(6) nonbonding distance is 3.201 (6) Å. However, the bonding within these acetyl ligands is symmetrical to within a $\pm 1\sigma$ limit. The average values of the Re–C(acyl), C(acyl)–O, and C(acyl)–C(methyl) distances are 2.182 (6), 1.239 (9), and 1.51 (2) Å, respectively. The average values of the C–H distances on C(7) and C(8) are 1.0 (1) and 0.94 (20) Å, respectively.

The central angle C(5)–Re–C(6) of 88.0 (3)° is not greatly different from the values of 86.5 (6) and 87.1 (4)° for the analogous angle in the rhenaacetylacetone molecule, [*cis*-$(OC)_4Re(CH_3CO)_2]H$, as determined respectively from X-ray[16] and neutron diffraction.[17] The sums of the angles about C(5) and C(6) are 360.0°, indicating planar hybridization at these acyl carbon atoms. Pyramidal hybridization about the methyl carbons C(7) and C(8) is reflected in the average value of the 12 H–C–H angles of 109 (9)°.

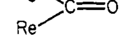
The benzamidinium cation has the expected structure. A delocalized π-electron system over the atoms C(10), N(1), and N(2) is evident. The average C–N distance of 1.308 (8) Å indicates considerable multiple-bond character. The sums of the angles about C(10), N(1), and N(2) are 360.0, 358, and 358°, respectively, and indicate essentially planar hybridization about these atoms. The C(10)–C(11) distance of 1.488 (9) Å represents a normal $C(sp^2)$–$C(sp^2)$ single-bond distance. Within the phenyl group, the average value for the C–C and C–H distances are 1.38 (2) and 1.01 Å, respectively. The sum of the six internal angles within the phenyl ring is 720.1°. The average value of the four N–H distances is 0.98 (11) Å.

Each organometallic anion participates in asymmetrical O···H–N hydrogen bonding to two adjacent cations, thereby forming a chain network of hydrogen bonds. For a given organometallic anion, the acetyl oxygen atom O(6) is hydrogen bonded to the N(1)–H(1) hydrogen atom of an adjacent cation, while the other acetyl oxygen atom O(5) is hydrogen bonded to the N(2)–H(3) hydrogen atom of a second adjacent cation. A figure showing these hydrogen-bonding interactions is included in the supplementary material. In the O(6)···H(1)–N(1) hydrogen bond, the values of the O···H, H–N, and O···N distances and the O–H–N angle are 1.87 (10) Å, 1.04 (10) Å, 2.898 (6) Å, and 167 (10)°, respectively. In the O(5)···H(3)–N(2) hydrogen bond, the corresponding values are 1.93 (7) Å, 1.02 (7) Å, 2.877 (8) Å, and 153 (4)°, respectively. These O···H–N hydrogen bonds represent normal hydrogen bonds, i.e. neither particularly strong nor unusually weak interactions. Normal O···N distances for hydrogen bonds of this type are ca. 2.89 Å[18] and have values usually found within the range of 2.93 ± 0.11 Å.[19]

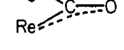
Discussion

One aspect of this work of possible interest to the synthetic and structural organometallic chemist is the use of the benzamidinium cation for the isolation of an anionic organometallic complex. The benzamidinium salt, **2**, crystallizes readily from solution. It is soluble in polar organic solvents, and the solid is very air-stable. Perhaps the benzamidinium cation would be a useful substitute for the PPN cation in other organometallic salts.

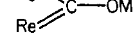
Table IV shows a listing of Re–C and C–O distances for acetyl ligands in rhena β-diketonate complexes and related molecules. This series of complexes includes examples of distinct acetyl ligands, **3**, acetyl ligands that are involved in delocalized bonding, **4**, and acetyl ligands that have considerable carbenoid ligand character, **5**. On going from an acetyl ligand of type **3** to type **5**, the Re–C distance should decrease and the acetyl C–O distance should increase.



3



4



5

In complexes **6**–**8**, the acetyl ligands are essentially electronically isolated ligands. Within this series, the Re–C and acetyl C–O distances are equivalent at a $\pm 1\sigma$ level. Complex **6** has the most precisely determined structure. The Re–C and acetyl C–O distances of **6** are 2.211 (6) and 1.214 (7) Å, respectively. The corresponding distances of (*p*-chlorobenzoyl)pentacarbonylrhenium are 2.22 (1) and 1.16 (2) Å.[24] A Re–$C(sp^2)$ distance of 2.21 Å is slightly shorter than is an estimated value for a single-bond distance. The Re–CH_3 distance in $CH_3Re(CO)_5$ is 2.31 (2) Å;[25] correcting this dis-

---

(16) Lukehart, C. M.; Zeile, J. V. *J. Am. Chem. Soc.* **1976**, *98*, 2365–2367.

(17) Schultz, A. J.; Srinivasan, K.; Teller, R. G.; Williams, J. M.; Lukehart, C. M. *J. Am. Chem. Soc.* **1984**, *106*, 999–1003.

(18) Olovsson, I.; Jönsson, P.-G. In "The Hydrogen Bond. Structure and Spectroscopy"; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland Publishing Co.: Amsterdam, 1976; Vol. II, pp 395–456.

(19) Joesten, M. D.; Schaad, L. J. In "Hydrogen Bonding"; Marcel Dekker, Inc.: New York, 1974.

(20) Lukehart, C. M.; Zeile, J. V. *J. Organomet. Chem.* **1977**, *140*, 309–316.

(21) Lenhert, P. G.; Lukehart, C. M.; Warfield, L. T. *Inorg. Chem.* **1980**, *19*, 311–315.

(22) Lukehart, C. M.; Warfield, L. T. *Inorg. Chim. Acta* **1980**, *41*, 105–110.

(23) Baskar, A. J.; Lukehart, C. M. *J. Organomet. Chem.* **1983**, *254*, 149–157.

(24) Astakhova, I. S.; Johnsson, A. A.; Semion, V. A.; Struchkov, Yu. T.; Anisiman, K. N.; Kolovoba, N. E. *J. Chem. Soc. D* **1969**, 488.

(25) Rankin, D. W. H.; Robertson, A. *J. Organomet. Chem.* **1976**, *105*, 331–340.

tance for the change in hybridization at the carbon atom gives as estimated Re–C(sp^2) single-bond distance of 2.28 (2) Å. Presumably, some degree of back-bonding of electron density from the Re atom to the acetyl ligands shortens the Re–C(acetyl) distance by ca. 0.07 Å. Furthermore, the acetyl C–O distance of 1.214 (7) Å in **6** is identical with the C–O distance of 1.214 (5) Å in acetaldehyde.[26]

In complexes **9–11**, the acetyl ligands are involved in a delocalized rhena β-diketonate ring system. The structures of **9** and **11** are determined to higher precision than those of **10**. In the rhenaacetylacetonate anion **9**, the average values of the Re–C and the acetyl C–O distances of 2.182 (6) and 1.239 (9) Å, respectively, indicate that the Re–C distance has decreased by 0.029 Å and the acetyl C–O distance has increased by 0.025 Å relative to those distances observed in **6**. For the copper complex **11**, the average Re–C and acetyl C–O distances are 2.153 (4) and 1.245 (6) Å, respectively. Relative to the corresponding distances in **6**, the average Re–C distance of **11** has decreased by 0.058 Å, while the average acetyl C–O distance of **11** has increased by 0.031 Å. These structural changes are consistent with a more delocalized structure such as **4**. The acetyl C–O distance in **11** is essentially the same as the ketonic C–O distance of 1.243 (7) Å in formamide.[26]

In the triacetylrhenato complexes **12** and **13**, the average values of the Re–C and acetyl C–O distances are 2.01 (3) and 1.37 (3) Å. Although these standard deviations are quite large, these acetyl ligands are presumably described best by the carbenoid structural type **5**. This Re–C distance is nearly the same as a Re–C distance to terminal carbonyl ligands, and the acetyl C–O distance is midway between the values of the longer C–O distance in organic esters, 1.312 (5) Å, and the C–O distance in saturated alcohols, 1.426 (5) Å.[26]

Other metalla β-diketonate complexes have structures consistent with structural type **4**. In $[cis\text{-}(OC)_4Mn(CH_3CO)_2]_3Al$, the average acetyl C–O distance is 1.251 (9) Å, and in $[(\eta\text{-}C_5H_5)(OC)Fe(i\text{-}PrCO)(CH_3CO)]BF_2$, the acetyl C–O distance is 1.291 (2) Å.[27,28] Both complexes have metal–acetyl carbon distances that indicate significant multiple bonding character, also.

On the basis of this selected comparison, the acetyl C–O distance of μ-η^2-acetyl ligands (which act as oxygen donors to a Lewis acid) will probably fall in the range 1.25–1.42 Å. Most acetyl C–O distances of this type will generally fall in the range 1.25–1.29 Å. An increase in the acetyl C–O distance will usually be accompanied by a concomitant decrease in the metal–acetyl carbon distance. Presumably, electron-rich metal atoms will afford more basic acyl oxygen atoms, and this aspect will be reflected in longer acyl C–O distances.

Structural effects due solely to the nature of the Lewis acid are difficult to assess from these data. The relevant distances of **10** and **11** cannot be compared because of the low precision of the structural determination of **10**. The small changes in the acetyl C–O distances (and the Re–C distances) on going from **9** to **11** are consistent with a slight shift toward a carbenoid structure for **11**. This type of structural change is expected when the acetyl ligands bond strongly to a central coordinating Lewis acid. However, the difference in acetyl C–O distances for **9** and **11** are within 1 esd.

Acknowledgment. C.M.L. thanks the National Science Foundation (Grant No. CHE-8106140), the Petroleum Research Fund, administered by the American Chemical Society, and the University Research Council of Vanderbilt University for support of this research. C.M.L. also acknowledges support from the Alfred P. Sloan Foundation as a Research Fellow. P.G.L. acknowledges support from the NIH BRSG (Grant No. RR07089-13).

Supplementary Material Available: Complete listing of final positional and thermal parameters and final observed and calculated structure factors and a labeled ORTEP diagram showing the O···H–N hydrogen bonding between the organometallic anion and two adjacent cations (32 pages). Ordering information is given on any current masthead page.

---

[26] *Spec. Publ.—Chem. Soc.* **1965**, *No. 18.*

[27] Lukehart, C. M.; Torrence, G. P.; Zeile, J. V. *J. Am. Chem. Soc.* **1975**, *97*, 6903–6904.

[28] Lenhert, G. P.; Lukehart, C. M.; Warfield, L. T. *Inorg. Chem.* **1980**, *19*, 2343–2347.