using a partial QS value assigned for the phenyl group. Results are generally in accord with known structural data,[1,2,40] but exceptions are known.[41,42] The model assumes that there will be no QS sign inversion in the systems being compared and that the partial QS values for the ligands will be negligible compared to that of the phenyl group whose value must remain constant over the range of compounds studied. Some recorded QS values exceed those predicting linear C–Sn–C angles,[43,44] indicating breakdown of the model. No partial QS value is available for the biphenyl group, but using the value for phenyl yields 126.6° for the carbon–tin–carbon angle (vs. 130.8° measured), an error of only 4.2° or 3.2%.

Acknowledgment. Our work is supported by the Office of Naval Research. We thank M&T Chemicals for the donation of organotin starting materials.

Registry No. $(C_6H_5C_6H_4)_2SnCl_2$, 92622-88-3.

Supplementary Material Available: Tables of IR and Raman data, thermal parameters, hydrogen atom data, equations of planes, and structure factors (33 pages). Ordering information is given on any current masthead page.

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Structure and Reactivity of Bridging Dimanganese and -rhenium Ethane-1,2-dionyl Compounds

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The synthesis, spectroscopic properties, and reactivity of binuclear manganese and rhenium compounds in which the metals are linked by an ethane-1,2-dionyl bridge are described. The compounds $M(CO)_5C({=}O)C({=}O)M(CO)_5$ (M = Mn, Re) are prepared by treatment of the respective pentacarbonyl anions with oxalyl chloride. These complexes have been characterized by ^{13}C NMR, IR, UV/visible, and mass spectrometries and, in the case of M = Re, by an X-ray diffraction study. $Re(CO)_5C({=}O)C({=}O)Re(CO)_5$ crystallizes in space group $P2_1/c$ and has unit cell dimensions a = 5.627 (4) Å, b = 12.392 (6) Å, c = 10.192 (6) Å, and β = 95.69 (8)° with Z = 2. Molecules of the complex lie such that the midpoint of the central C–C bond coincides with a crystallographic inversion center. The central Re–CO–CO–Re unit is planar, with the $Re(CO)_5$ substituents mutually trans and staggered relative to the ethane-1,2-dionyl plane. The dionyl C–Re bonds are of length appropriate to $Re–C_{sp^2}$ single bonds, 2.228 (12) Å, and the central C–C bond is also single, length 1.558 (21) Å. Attempts to convert the ethane-1,2-dionyl moiety, which can be regarded as two carbon–carbon coupled CO molecules, into C_2 oxygenates have not met with much success, either in catalytic or in stoichiometric reactions. Decomposition of the $M_2(CO)_{12}$ species to $M_2(CO)_{10}$ + 2CO (M = Mn, Re) is the preferred reaction in all cases. Aspects of the reactivity of $M(CO)_5C({=}O)C({=}O)M(CO)_5$ (M = Mn, Re) toward hydride donor reagents, hydrogen, and neopentyllithium are reported.

Introduction

From an industrial point of view, selectivity in conversion of syngas to C_2 products remains a major objective and is therefore a subject of much research.

To date the most generally accepted mechanism in CO hydrogenation involves the initial reduction of a coordinated CO ligand followed by CO insertion, subsequent reduction, and product formation via hydrogenation.[1,2] Mechanisms and examples of reactions involving carbon–carbon bond formation between two CO molecules as a first step and hydrogenation as a second step are much less common despite the fact that, in terms of prospects for C_2 selectivity, this approach looks promising.

An obvious structure resulting from a CO-to-CO coupling would be a compound with an ethane-1,2-dionyl bridge, e.g., $L_nMC({=}O)C({=}O)ML_n$. In organotransition-metal chemistry neither such compounds nor reactions leading to them are known, although speculations about their possible existence and relevance in catalysis have been put forward by Wilkinson et al.[3]

Examples that bear an important resemblance are the coupling of CO ligands by low valency zirconium compounds reported by Bercaw et al.,[4] the reductive coupling of isocyanide ligands in molybdenum and tungsten complexes reported by Lippard et al.,[5] and, possibly, the coupling of CO ligands in highly reduced metal carbonyls.[6]

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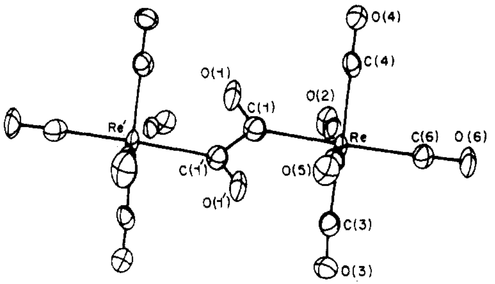
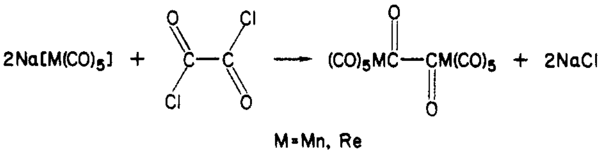


Figure 1. Molecular geometry of $Re(CO)_5C({=}O)C({=}O)Re(CO)_5$ showing vibrational ellipsoids drawn to enclose 50% probability density. The labeling scheme is indicated.

We report in this paper the synthesis and full characterization of the compounds $(CO)_5MC({=}O)C({=}O)M(CO)_5$ (M = Mn, Re). The formation and existence of such species under "catalytic" conditions will be discussed.

Results

Synthesis. The ethane-1,2-dionyl compounds $M_2(CO)_{12}$ are readily prepared by metathesis of $Na[M(CO)_5]$ with oxalyl chloride in diethyl ether (eq 1). Pure compounds



$$2Na[M(CO)_5] + ClC(O)C(O)Cl \longrightarrow (CO)_5MC(O)C(O)M(CO)_5 + 2NaCl \quad (1)$$

M=Mn, Re

are obtained by recrystallization from CH_2Cl_2 and appear to be only slightly air sensitive. In solution and in the solid state decomposition occurs to $M_2(CO)_{10}$. $Mn_2(CO)_{12}$ in particular is sensitive to decomposition in solution; e.g., in tetrahydrofuran (THF) decomposition takes place above -20 °C.

Other well-known anions such as $CpMo(CO)_3^-$, $CpFe(CO)_2^-$, and $Co(CO)_4^-$ were investigated; however, the products of reaction with oxalyl chloride did not show sufficient stability to allow isolation.

Crystal and Molecular Structure of $Re(CO)_5C({=}O)C({=}O)Re(CO)_5$. The results of the X-ray crystal structure analysis of $Re(CO)_5C({=}O)C({=}O)Re(CO)_5$ at 220 K are presented in Tables I and II that list the atomic positional parameters and the derived bond lengths and interbond angles, respectively. Figures 1 and 2 show the molecular geometry and the atomic labeling scheme employed. Crystals of $Mn(CO)_5C({=}O)C({=}O)Mn(CO)_5$ proved too unstable for X-ray analysis.

Table I. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $Re(CO)_5C({=}O)C({=}O)Re(CO)_5$ at 200 K

	x	y	z	U^a
Re	2269 (1)	854 (1)	2106 (1)	29 (1)
C(1)	776 (17)	478 (10)	98 (12)	39 (4)
O(1)	1086 (14)	987 (7)	-901 (8)	50 (3)
C(2)	3083 (19)	-709 (10)	2262 (11)	36 (4)
O(2)	3539 (14)	-1586 (7)	2325 (9)	51 (3)
C(3)	-314 (18)	547 (9)	2923 (13)	39 (4)
O(3)	-1742 (13)	391 (8)	3476 (10)	50 (3)
C(4)	4777 (18)	1176 (9)	1201 (12)	38 (4)
O(4)	6207 (13)	1327 (7)	676 (8)	44 (3)
C(5)	1172 (16)	2340 (9)	1618 (11)	35 (4)
O(5)	463 (14)	3120 (7)	1244 (9)	50 (3)
C(6)	3728 (19)	1258 (10)	3885 (14)	43 (4)
O(6)	4530 (14)	1469 (8)	4873 (9)	54 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

These results unequivocally identify $Re_2(CO)_{12}$ as being an ethane-1,2-dionyl-bridged dimetal species. The dionyl (C_2O_2) moiety is strictly planar, with the $Re(CO)_5$ substituents mutually trans, and lies on a crystallographic inversion center. The molecule as a whole possesses strict C_i symmetry and approximate C_{2h} symmetry. In the crystal structure molecules are separated by normal van der Waals distances, the shortest of which are O(3)···O(5″) = 2.940 Å (O(5″) being related to O(5) by $-x, {}^1/_2 + y, {}^1/_2 - z$) and O(2)···O(6″) = 3.008 Å (O(6″) being related to O(6) by $1 - x, -y, 1 - z$).

The geometry of the dionyl and metal fragments may be usefully compared with those of rhenium acyl, alkyl, and alkylidene complexes. Thus the Re–C(1) distance is 2.228 (12) Å,[7] which is similar to that in rhenium acyl

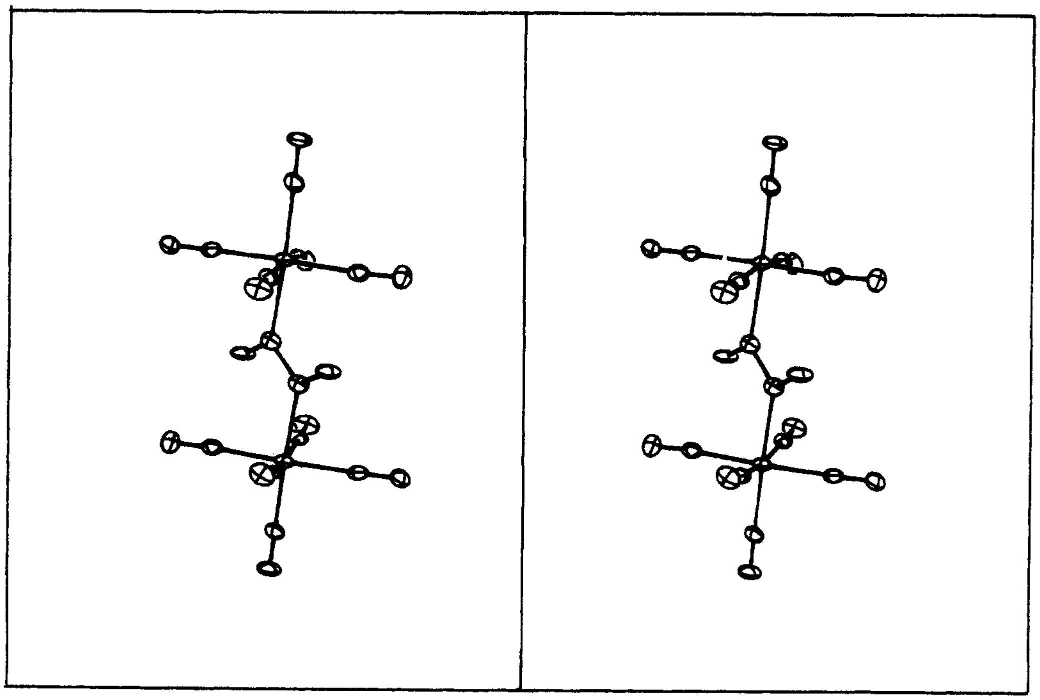


Figure 2. Stereoscopic illustration of the molecular geometry of $Re(CO)_5C({=}O)C({=}O)Re(CO)_5$.

Table II. Bond Lengths (Å) and Bond Angles (deg) of $Re(CO)_5C(=O)C(=O)Re(CO)_5$

Bond Lengths

Re-C(1)	2.228 (12)	C(4)-O(4)	1.137 (15)	Re-C(6)	2.025 (13)
Re-C(3)	1.989 (13)	C(6)-O(6)	1.119 (16)	C(1)-C(1′)	1.558 (23)
Re-C(5)	2.020 (11)	Re-C(2)	2.011 (12)	C(3)-O(3)	1.152 (16)
C(1)-O(1)	1.231 (15)	Re-C(4)	1.998 (12)	C(5)-O(5)	1.122 (14)
C(2)-O(2)	1.126 (15)				

Bond Angles

C(1)-Re-C(2)	87.6 (4)	Re-C(1)-C(1′)	119.7 (11)	C(4)-Re-C(5)	89.5 (5)
C(2)-Re-C(3)	90.7 (5)	Re-C(2)-O(2)	178.8 (11)	C(2)-Re-C(6)	94.0 (5)
C(2)-Re-C(4)	90.4 (5)	Re-C(4)-O(4)	177.9 (10)	C(4)-Re-C(6)	91.7 (5)
C(1)-Re-C(5)	81.5 (4)	Re-C(6)-O(6)	179.2 (9)	Re-C(1)-O(1)	124.0 (8)
C(3)-Re-C(5)	89.0 (5)	C(1)-Re-C(3)	91.5 (5)	O(1)-C(1)-C(1′)	116.2 (13)
C(1)-Re-C(6)	176.7 (5)	C(1)-Re-C(4)	85.5 (5)	Re-C(3)-O(3)	175.4 (11)
C(3)-Re-C(6)	90.9 (5)	C(3)-Re-C(4)	177.1 (5)	Re-C(5)-O(5)	173.4 (9)
C(5)-Re-C(6)	96.8 (5)	C(2)-Re-C(5)	169.1 (4)		

complexes such as $Re(CO)_4(PhNH_2)C(O)CH_3$[8] (2.216 (6) Å) and $Re(CO)_5C(O)C_6H_4Cl$[9] (2.22 (1) Å) and slightly shorter than Re–C_{sp^3} distances in $Re(CO)_5CH_2CH_2Re(CO)_5$[10] (2.30 (1) Å) and $Re(\eta^5\text{-}C_5H_5)(H)(CO)(CH_2Ph)$[11] (2.29 (1) Å) but rather longer than R═C_{sp^2} double bonds in $Re(CO)_4({=}C(OCH_3)CH_3)Mn(CO)_5$[12] (2.094 (7) Å) and $Re(\eta^5\text{-}C_5H_5)(CO)_2({=}CHSiMe_3)$[13] (1.92 (2) Å). In addition, the dionyl C–O distance (C(1)–O(1) = 1.231 (15) Å) is very close to those observed in the acyl complexes mentioned above (1.214 (7) and 1.16 (1) Å, respectively). The planarity of the $Re_2C_2O_2$ unit is perfect to within experimental error (maximum deviation for C(1), 0.002 Å; torsion angle Re–C(1)–C(1′)–O(1′) = 0.4 (10)°). This might be taken to imply some π overlap between the sp^2-hybridized acyl carbons. Any such overlap does not, however, lead to any shortening of the C(1)–C(1′) bond, which is similar to observations with respect to other α,β-diketones (e.g., C(O)–C(O) = 1.542 (3) Å in benzil,[14] where the O–C–C–O torsion angle is 108.2 (3)°; cf. 1.56 (3) Å here). The two $Re(CO_5)$ fragments are mutually eclipsed and staggered with respect to the dionyl moiety. Thus the angles between the dionyl $Re_2C_2O_2$ plane and the Re, C(6),C(2),C(5),C(1) and Re,C(1),C(6),C(3),C(4) planes are 38.8 and 51.9°, respectively. The dionyl ligand appears, therefore, to function as a typical acyl ligand to each $Re(CO)_5$ moiety when acting as a bridging ligand in this way; there is no indication of any localized carbenoid, multiple, Re–C bonding in this complex.

The coordination geometry around the rhenium atoms is distorted in an interesting way, the equatorial (CO)–Re–C(1) and cis-(CO)–Re–C(6) angles varying considerably (the former between 81.5 (4) and 91.9 (5)° and the latter between 90.9 (5) and 96.8 (3)°). The cause of these angular distortions appears to be nonbonded interactions between the β-keto oxygen O(1′) and the equatorial CO ligands C(3) and C(2) (O(1′)···C(3) = 2.813 Å and O(1′)···C(2) = 2.949 Å). These interactions cause the C(1)–Re–C(2,3) angles to increase (C(1)–Re–C(3) = 91.9 (5) and C(1)–Re–C(2) = 87.6 (4)°; cf. (C(1)–Re–C(4) = 85.5 (5) and C(1)–Re–C(5) = 81.5 (4)°). The C(6)–Re–C(*n*) angles show a related pattern of distortion (C(6)–Re–C(2) = 94.0 (5), C(6)–Re–C(3) = 90.9 (5), C(6)–Re–C(4) = 91.7 (5), and C(6)–Re–C(5) = 96.8(5)°). Clearly, the angular distortions induced by these nonbonded interactions are coupled to one another. The electronic factors behind this coupling have been discussed by Elian and Hoffmann.[15]

Table III. Spectroscopic Properties of Compounds $M_2(CO)_{12}$ (M = Mn and Re)

	Mn	Re	
IR, cm^{-1}	2100	2125	$M(CO)_5$ C_{4v}
	2025	2035	
	2005	2002	
	1670	1652	>=O
		1624	
		1562	
^{13}C NMR, δ	209 br	182.6 ax	M=C=O
		184.1 eq	
	256.0	253.3	>=O
UV/vis, nm	506	533	
PPNIDCI, *m/e*	223 (base peak)		$M(CO)_6^+$
	447 (parent, 90%)		$M_2(CO)_{12}H^+$
	195		$M(CO)_5^-$

Spectroscopic Data. The IR, ^{13}C NMR, UV (visible spectrum), and mass spectroscopy (PPNIDCI) data are listed in Table III. All data are consistent with the X-ray structure.

The three IR bands in the 1900–2150 cm^{-1} region for both compounds are in agreement with a $M(CO)_5$ fragment of C_{4v} symmetry. The other important features of the spectra are the bands in the 1700–1550 cm^{-1} region, which are assigned to the dionyl ligand.

The ^{13}C NMR spectra show, in addition to the resonances of the terminal CO ligands, a resonance of the dionyl carbon atoms at approximately δ 255. This is in the same range as found for other metal acyl compounds.[16]

Mass spectroscopic analysis of $(\overline{Mn(CO)_5)_2C(O)C(O)}$ (with soft ioninizing gases like isobutane) shows a high-intensity parent peak (90%) in the positive ion spectra at *m/e* 447 ($Mn_2C_{12}O_{12}H^+$), in accordance with its bimetallic formulation. The base peak is observed at *m/e* 223 ($MnC_6O_6^+$). In the negative ion spectra the parent and base peak is observed at *m/e* 195 ($MnC_5O_5^-$). No peaks at higher *m/e* values are observed.

The UV spectra of the compounds show absorptions at 361 and 506 nm for the manganese complex and absorp-

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(7) Estimated standard deviations in the least significant digit are given in parentheses here and throughout this paper.

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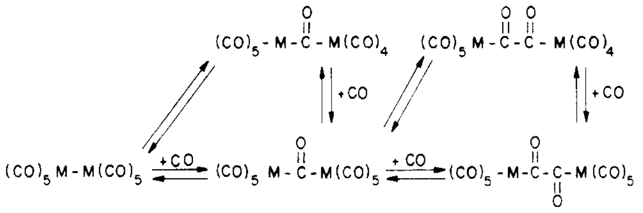
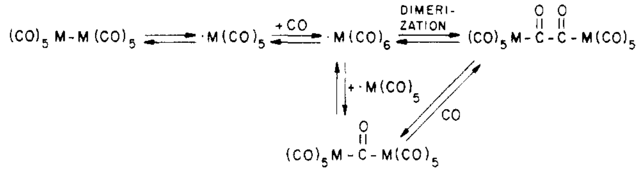
Scheme I



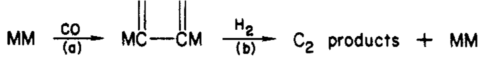
Scheme II



tions at 384 and 535 nm for the rhenium complex. The long wavelength absorptions are ascribed to a charge-transfer band between the metal carbonyl and the dionyl fragment in the same way as has been suggested by Casey et al. for the compounds $(CO)_5MnC(=O)C(=O)R$.[17] Owing to the cooperative effect of the presence of two metal carbonyl fragments and the higher symmetry of the complexes, the shift to longer wavelength becomes larger in the dionyl complexes.

In the light of the similarity in spectroscopic data, $[Mn_2(CO)_{10}]C(O)C(O)$ will have a structure similar to that of $[Re_2(CO)_{10}]C(O)C(O)$.

Reactions of 1,2-Dimetallaethane-1,2-dionyl Complexes. In the Introduction we mentioned the carbon–carbon bond formation between two CO molecules as a novel starting point for syngas conversions with high selectivity. If 1,2-dimetallaethane-1,2-dionyl complexes, the obvious structure resulting from a CO-to-CO coupling, were to be intermediates in syngas conversions, two important reactions have to be considered: (a) their formation from dimetallic compounds with CO and (b) their subsequent reactions with H_2 (eq 2).



$$MM \xrightarrow[(a)]{CO} M\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}M \xrightarrow[(b)]{H_2} C_2 \text{ products} + MM \tag{2}$$

The characterization and isolation of the ethane-1,2-dionyl complexes gave us the opportunity to study their reactivity, in particular that of the more stable $Re_2(CO)_{12}$, with respect to reactions a and b.

Decomposition/Formation of $[M_2(CO)_{10}]C(O)C(O)$. For the decomposition and formation of $Re_2(CO)_{12}$ from $Re_2(CO)_{10}$ and CO two modes can be envisaged: a stepwise CO insertion/extrusion pathway[18] (Scheme I) and a radical pathway (Scheme II).

Reacting $Re_2(CO)_{10}$ with CO (at 100 bar) in THF for several days at 35 °C did not result in the formation of $Re_2(CO)_{12}$ at any detectable yield (IR).

Decomposition of $Re_2(CO)_{12}$ to $Re_2(CO)_{10}$ is complete in 3 days at room temperature under nitrogen. Interestingly, under CO considerable inhibition occurs: at 40 bar no detectable decomposition takes place in 7 days, whereas at 2 bar of CO 60% decomposition takes place in 16 days. During decomposition no intermediates were observed. Following decomposition by EPR under various conditions, with and without spin trap, no signal was detected.

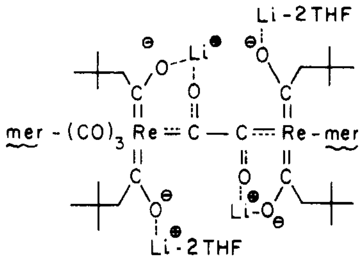
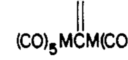


Figure 3. Structure of the reaction product from treatment of $Re(CO)_5C(=O)C(=O)Re(CO)_5$ with 4 equiv of neo-$C_5H_{11}Li$ in THF.

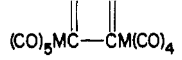
The above data indicate that, under the conditions employed, $Re_2(CO)_{10}$ is not in equilibrium with $Re_2(CO)_{12}$.

Although we cannot convert $Re_2(CO)_{10}$ into the dione, it is possible to suppress the reverse reaction by CO. The most reasonable explanation for this kinetic stability of the dione compound is that decomposition occurs in a stepwise manner, e.g., Scheme I. The "$M_2(CO)_{11}$" that forms as an intermediate reacts rapidly with CO at 40 bar, preventing the thermodynamically favored decomposition. Two structures can be envisaged for "$M_2(CO)_{11}$":



$$(CO)_5M\overset{O}{\overset{\|}{C}}M(CO)_5$$

A



$$(CO)_5M\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}M(CO)_4$$

B

Recombination of the latter complex B with CO should be very rapid. Complex A would require a fast CO insertion. Reactions involving CO insertion into a bridged carbonyl are not known. However, note that most bridging carbonyls are accompanied by metal–metal bonds and that, in the closely related bridging methylene complexes, CO insertion occurs readily in the absence of metal–metal bonding,[19] in contrast to the inertness of the metal–carbon bond in the presence of a metal–metal bond.[20]

Further decomposition of "$M_2(CO)_{11}$" in the absence of CO yields $M_2(CO)_{10}$ rapidly via similar pathways. From the above experiments we conclude that the formation of the dionyl complex from the metal decacarbonyls is thermodynamically unfavorable at pressures below 100 bar. The strength of the Re–Re bond in $Re_2(CO)_{10}$ may, both in the thermodynamic and the kinetic sense, play an important role.

Reactivity of $M_2(CO)_{10}C(O)C(O)$ toward Hydrogen and Other Organic Substrates. In studying the reactivity of the 1,2-dimetallaethane-1,2-dionyl complexes, emphasis was placed on the reactivity of the dionyl bridge, in particular its hydrogenation.

Catalytic hydrogenation was attempted, e.g., $(Mn_2(CO)_{10})C(O)C(O)$ with $Co_2(CO)_8$ under CO/H_2 (100 bar) at 60 °C and $(Re_2(CO)_{10})C(O)C(O)$ with cationic Rh–phosphine complexes under H_2 (20 bar) at 30 °C.[21] However, none of the reactions yielded products that indicated reaction of the ethane-1,2-dionyl bridge.

Similar conclusions can be drawn from the stoichiometric hydrogenation of $(Re_2(CO)_{10}C(O)C(O)$ by hydride donors. In all cases decomposition occurs and $Re_2(CO)_{10}$

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and [Re–CO] anions are the major products. Only in the case of very strong H^- donors like $LiAlH_4$ in THF, C_1, C_2, and C_4 products are observed. However, a nearly similar product distribution is observed when $Re_2(CO)_{10}$ is used, instead. Furthermore the rhenium compound was found to be resistant to hydrogenation by AlH_3 and BH_3 although slow decomposition to $Re_2(CO)_{10}$ occurred.

Other typical reactions of α-diketones, such as Wittig reactions or cyclization reactions with $P(OCH_3)_3$, do not occur. For example, in the former reactions with $Ph_3PC(H)$-*t*-Bu, decomposition occurs and phosphonium salts are formed.

However, $(\overline{\mathrm{Re}_2(\mathrm{CO})_{10})\mathrm{C(O)C}}(\mathrm{O})$ reacts without decomposition with 4 equivalents of neopentyllithium in THF. On the basis of ^1H and ^{13}C NMR and IR the structure given in Figure 3 is proposed for this complex.[22] Two coordinated molecules of THF per rhenium are present, and they appear to be essential for the stability of the complex.

The most interesting feature of the spectroscopic data is the broad resonance at δ 294.1 in the ^{13}C NMR spectrum. It is ascribed to the carbons of the ethane-1,2-dionyl bridge and is shifted approximately 40 ppm downfield from that in the parent dionyl complex, close to the carbenoid region. This fact, in combination with the broadness of the signal, suggests that the dionyl bridge is still intact and is involved in a competitive coordination of the Li^+ ion with THF. The presence of a band at 1551 cm^{-1} in the IR spectra is another indication that the dionyl bridge is still intact and is involved in coordination.

One of the reasons why, in this particular reaction, the dionyl bridge remains intact could be the increase of bond order of the rhenium dionyl carbon band due to the coordination of the lithium cation, which induces a carbenoid character.[20] Another reason may be that the *mer* geometry and anionic character of the compound makes CO dissociation more difficult.

In general, the reactivity of the terminal CO ligands is higher than that of the ethane-1,2-dionyl bridge. The reasons for this may well be both steric and electronic.

Conclusions

This study has shown that compounds containing two carbon–carbon coupled C=O units in the form of 1,2-dimetallaethane-1,2-dionyl complexes can exist. However, direct synthesis of such compounds from CO and metal carbonyls is not very likely in the case of the two metals studied here (Re and Mn). Still, formation of such species in small quantities at high CO pressures cannot be excluded, and some intermediacy in reactions leading selectively to C_2 oxygenates from syngas remains an attractive possibility.

At present, hydrogenation of the ethane-1,2-dionyl ligand to C_2 oxygenates is not possible by simple methods. Instead, in the rhenium complex the terminal CO ligands appear to be more reactive than the bridge.

Experimental Section

(1) General Remarks. All reactions were carried out in an argon or a nitrogen atmosphere with Schlenk-type glassware. Prior to use, solvents were distilled from sodium ketyl (THF, diethyl ether); $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were used as purchased (Ventron, Aldrich). The $NaM(CO)_5$ compounds (M = Mn, Re) were prepared by sodium/mercury reduction of $M_2(CO)_{10}$ in THF and subsequent evaporation of the solvent. The residual THF was determined by ^1H NMR. All commercially available chemicals were used as purchased (Aldrich, Ventron). The remaining compounds were prepared according to the references mentioned.

^{13}C NMR spectra were recorded on a Bruker WM-250, ^1H NMR spectra on a Bruker HR-90, and EPR spectra on a Varian E-104 A. (In the irradiation experiments a Philips 375-W IR lamp was used as a light source.) PPNIDCI spectra were recorded on a Finigar TSQ mass spectrometer. IR spectra were measured in CH_2Cl_2 solutions on a Perkin-Elmer 599 spectrophotometer.

Samples for the various characterization methods were made up by glovebox techniques.

GC analyses were performed on Hewlett-Packard 5840 and 5880 gas chromatographs. Chrompack CpSi15 capillary columns were used for liquid-phase analysis. Gas phases were analysed over a PORAPAK R 80-100 mesh 12 × $^1/_8$ column.

X-ray analysis was performed at the University of Bristol, Bristol, UK.

(2) Preparation of $[\overline{\mathbf{M}_2(\mathbf{CO})_{10}]\mathbf{C(O)C}}(\mathbf{O})$. M = Mn. Half of an equivalent of oxalyl chloride in diethyl ether was added slowly to a slurry of $NaMn(CO)_5$ in diethyl ether at −78 °C. The reaction mixture turned purple and was slowly warmed to 0 °C. After evaporation of the solvent, the residue was extracted and recrystallized from CH_2Cl_2 by stirring for a very short period at room temperature and rapidly filtering. The resulting deep purple, bricklike crystals were separated from the mother liquor by decanting and subsequently isolated after being dried under vacuum at 0 °C (yield >50%).

M = Re. The same procedure was followed as for $Mn_2(CO)_{12}$ with the difference that the compound is much more stable and slower handling at room temperature is not penalized by lower yields. Both compounds should be stored under inert atmosphere at <−20 °C.

(3) Formation/Decomposition Reactions. EPR Measurements. Solutions of low concentrations of both $Mn_2(CO)_{12}$ and $Re_2(CO)_{12}$ were made, and spectra were run while decomposition took place at room temperature. Wide-scan spectra did not show any resonances. Narrowing scan ranges to 200 Hz gave similar results for both compounds.

Neither photolysis at −20 °C nor addition of spin trap ($(CH_3)_5C_6NO$ for $Mn_2(CO)_{12}$ and t-C_4H_9NO for $Re_2(CO)_{12}$) and following the same procedure as mentioned above resulted in resonances.

Photolysis at −20 °C and room temperature in the presence of spin trap yielded spectra that can be assigned to $M(CO)_5$ spin-trap radicals (based on *g* values, splitting patterns, and comparison with spectra starting from $M_2(CO)_{10}$). Longer irradiation gave other radical products that we assign to organic decomposition products that lack splitting patterns due to the metals.

Decomposition/Formation under CO or N_2. During initial experiments it was found that even small amounts of water catalyze decomposition of $M_2(CO)_{12}$ via the water gas shift reaction. Very carefully cleaned and dried glassware has to be used in these decompositions to obtain clean reactions. In addition, reactions in THF are preferred to reactions in CH_2Cl_2 owing to other decompositions. Decompositions were monitored by IR, and conversions were estimated by following the decrease of $M_2(CO)_{12}$ and increase of $M_2(CO)_{10}$ absorptions at time intervals. Concentration vs. intensity graphs were made in advance.

Decomposition under N_2 was carried out in the glovebox. Decompositions under CO were performed in Hastelloy autoclaves with glass liners. Pressures were measured by using gauges with digital displays. Spectra were taken from solutions under 1 bar of CO and immediately after sample makeup.

Reaction of $[\overline{\mathbf{Re}_2(\mathbf{CO})_{10}\mathbf{C(O)C}}(\mathbf{O})$ with Neopentyllithium. A 192-mg sample of $Re_2(CO)_{12}$ and 85.5 mg of $C_5H_{11}Li$ were placed in a Schlenk vessel, and 8 mL of THF was added at −78 °C while the solution was stirred. After 5 min the mixture was slowly warmed to room temperature. A yellow solution resulted. The solvent was removed under vacuum at room temperature and the resulting powder collected: ^1H NMR (CD_2Cl_2) δ 3.47 (J = 12 Hz, 1), 1.98 (J = 12 Hz, 1) (AX quartet), 2.47 (AB quartet), 0.80 (s, 9), 0.95 (s, 9), 1.88, 3.82 (THF); ^{13}C NMR (CD_2Cl_2) δ 321.4, 316.5 (Re=C), 294.1 (C glyoxal), 209.2, 205.9, 202.6 (Re(CO)), 79.5 (CH_2), 31.5, 30.2 (CH_3), 32.3, 32.4 (Me_3C), 78.8, 25.9 (THF); IR (CD_2Cl_2, cm^{-1}) 2063 (vw), 1986 (s), 1975 (sh), 1884 (vs), 1830 (m), 1808 (sh)

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(terminal CO), 1551 (m), 1510–1410 (several not well-resolved bands of medium intensities).

Crystal Structure Determination of Re(CO)$_5$C(=O)C(=O)Re(CO)$_5$. Crystals data: $C_{12}O_{12}Re_2$; M_r = 708.4; monoclinic; space group $P2_1/c$ (No. 14); a = 6.527 (4) Å, b = 12.392 (6) Å, c = 10.192 (6) Å, β = 95.69 (8)°; U = 820.2 (7) Å^3; D_{calcd} = 2.87 g cm^{-3}; Z = 2; graphite-monochromated X radiation, $\bar{\lambda}$ = 0.710 69 Å, μ(Mo Kα) = 150.1 cm^{-1}.

A small crystal (ca. 0.18 × 0.2 × 0.3 mm) was mounted under N_2 in a thin-walled glass capillary for data collection. Data were collected at 220 K on a Nicolet P3m diffractometer, the low temperature being necessary to minimize crystal decomposition in the X-ray beam. A correction was applied for the ca. 20% decay that occurred during the course of the diffraction experiment. A total of 1576 intensity data were collected in the range $4° < 2\theta < 50°$ and corrected for absorption by an empirical method (based on 235 azimuthal scan data, transmission coefficients varied between 0.010 and 0.035). Of these, 1240 were unique observations of which 1168 with $F^2 > 2\sigma(F^2)$ were used in the structure solution and refinement. The structure was determined by conventional heavy-atom methods (Patterson and Fourier) and refined, with all atoms assigned anisotropic vibrational parameters, by blocked-cascade full-matrix least squares to final residual indices R = 0.038, R_w 0.038, and s = 1.32[23] (weights $w = (4\sigma(F_o^2)/F_o^2 + 0.0008F_o^2)^{-1}$ with $\sigma(F_o^2)$ based on counting statistics alone). A final difference electron density Fourier synthesis showed no features of magnitude >2.7 e Å^{-3}, the largest peaks being less than ca. 1 Å from the metal atoms.

Registry No. [$Mn_2(CO)_{10}$]C(O)C(O), 92641-65-1; [$Re_2(CO)_{10}$]C(O)C(O), 92641-66-2; [$Re_2(CO)_{10}$]C(O)C(O) *neo*-$C_5H_{11}Li$ derivative, 92641-68-4; $NaMn(CO)_5$, 13859-41-1; $NaRe(CO)_5$, 33634-75-2; $Re_2(CO)_{10}$, 14285-68-8; $Mn_2(CO)_{10}$, 10170-69-1; oxalyl chloride, 79-37-8.

Supplementary Material Available: Tables listing the anisotropic vibrational parameters and the observed and calculated structure factors (all structure determination calculations were carried out with programs of the Nicolet SHELXTL system on a Data General ECLIPSE (R) minicomputer; complex neutral atom scattering factors were taken from ref 24) (8 pages). Ordering information is given on any current masthead page.

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[23] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $S = [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^2$.

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Potential Application of (1,3-Dithiol-2-ylidene)metal Complexes to the Synthesis of Tetrathiafulvalene Derivatives

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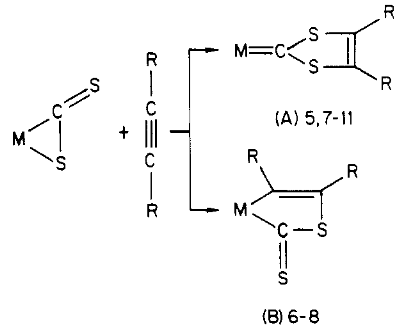
1,3-Dithiol-2-ylidene derivatives are obtained by reacting hexafluorobut-2-yne with the η^2-CS_2 complexes (triphos)Ni(η^2-CS_2) and (np$_3$)Ni(η^2-CS_2). The 1,3-dithiolium carbene ligand can be easily replaced by CO and $F_3CC{\equiv}CCF_3$ and, in turn, dimerizes to tetrakis(trifluoromethyl)tetrathiafulvalene (CF$_3$TTF). Some of the reactions reported present interesting catalytic aspects. The decomposition to air of the carbene complex (triphos)Ni[$CS_2C_2(CF_3)_2$] yields two dithiolene derivatives and CF$_3$TTF.

Introduction

Much current interest is presently being shown in the chemistry of η^2-CS_2 metal complexes. These compounds, in fact, can serve as precursors for a variety of sulfur-containing ligands or free products.[1-12]

A reaction of η^2-CS_2 complexes that could have interesting practical applications is the 1,3 dipolar cycloaddition of activated alkynes.[5-11] Depending on the nature of the metal fragment and of the coligands, alkynes can add to M–η^2-CS_2 in two different ways (Scheme I).

Scheme I



The potential applications of (1,3-dithiol-2-ylidene)metal derivatives of type A in the synthesis of sulfur-containing compounds appear to be very promising as shown in Scheme II.[11,13-15]

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