Organometallics 1991, *10*, 2173–2177

Unusual Mixed-Metal Carbonate-Bridged Complexes via Oxidation of a Carbonyl Ligand in $[RhM(CO)_4(Ph_2PCH_2PPh_2)_2]$ (M = Mn, Re) and $[IrRe(CO)_5(Ph_2PCH_2PPh_2)_2]$

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Received November 23, 1990

The complexes $[RhM(CO)_4(dppm)_2]$ (M = Mn (1), Re (2); dppm = $Ph_2PCH_2PPh_2$) and $[IrRe(CO)_5(dppm)_2]$ (3) react with molecular oxygen to give the corresponding carbonate complexes $[RhM(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (M = Mn (4), Re (5)) and $[IrRe(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (6). No intermediates were observed in these reactions even at −60 °C. The X-ray structure determination of compound 4 shows that the carbonate ligand bridges the metals in a unique $\mu_2\text{-}\eta^2$ fashion in which one oxygen atom bridges the metals and another is also bound in Mn leaving one oxygen uncoordinated. Compound 4 crystallizes in the monoclinic space group $C2/c$ with a = 35.591 (6) Å, b = 12.556 (3) Å, c = 25.277 (5) Å, β = 116.46 (2)°, V = 10112.8 Å^3, and Z = 8. The structure, which displays a 70:30 rotationally disordered "$RhMn(CO)_3(\mu\text{-}CO_3)$" moiety, has refined to R = 0.079 and R_w = 0.104 on the basis of 366 parameters refined and 2942 independent observations.

Introduction

The activation of molecular oxygen by transition-metal complexes is an area of considerable interest, in a large part owing to its relevance to the catalytic oxidation of organic substrates.[1-3] Complexes of the iron, cobalt, and nickel triads have played a dominant role in dioxygen activation, and a large number of species in which the dioxygen moiety is bound either terminally to one of these metals or bridging two metals, in either peroxo or superoxo formulations, have been characterized.[4-7] In many of these complexes the coordinated O_2 moiety has been shown to react with substrate molecules resulting in substrate oxidation by oxygen atom transfer.[8-14]

It has long been surprising to us that one well-known class of binuclear complexes of the above metals, those bridged by dppm ligands (dppm = $Ph_2PCH_2PPh_2$), have been rather unreactive with dioxygen. To our knowledge, $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$ appears to be the only documented O_2 adduct of this class,[15] although a related dioxygen adduct of $[IrCl(CO)(dppp)]_2$ (dppp = $Ph_2P(CH_2)_3PPh_2$), in which the metals are widely separated, has been reported.[16]

During investigations on the low-valent, mixed-metal complexes $[RhM(CO)_4(dppm)_2]$ (M = Mn, Re), it was noted that these species underwent facile oxidative addition reactions; even exposure of the RhRe complex to chlorinated solvents yielded the chloro-bridged species $[RhRe(CO)_3(\mu\text{-}Cl)_2(dppm)_2]$.[17] The reactions of these species with dioxygen were therefore carried out in attempts to obtain analogous oxidation products in which the coordinated dioxygen ligand could be viewed as a peroxo group, much as had been observed in $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$. The results of this study, in which we failed to observe simple O_2 adducts but instead observed the unusual, facile oxidation of a carbonyl ligand, are reported herein.

Experimental Section

General Considerations. All solvents were dried and deoxygenated before use and transferred directly to the reaction mixture by cannula. Reactions were conducted with use of standard Schlenk procedures. Prepurified argon was used without further drying or deoxygenating. Hydrated rhodium(III) chloride and iridium(III) chloride were obtained from Johnson Matthey Ltd., and $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ were purchased from Strem and sublimed before use. Bis(diphenylphosphino)methane (dppm) was obtained from Aldrich. The 99% carbon-13-enriched carbon monoxide was obtained from Isotec Inc., while O_2 was purchased from Matheson. The compounds $[RhMn(CO)_4(dppm)_2]$[18] (1), $[RhRe(CO)_4(dppm)_2]$[18] (2), $[IrCl(dppm)_2]$,[19] and $[PPN][Re(CO)_5]$[20] were all prepared according to the literature methods.

The ^1H, $^1H\{^{31}P\}$, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM-400 spectrometer, and infrared spectra were run on either a Nicolet 7199 Fourier transform interferometer or a Perkin-Elmer 883 spectrophotometer, either as solids (Nujol mulls on KBr disks) or solutions (KCl windows, 0.5-mm path length). Elemental analyses were performed by the microanalytical service within the department. Spectral data are summarized in Table I.

Preparation of Compounds. (a) $[IrRe(CO)_5(dppm)_2]$ (3). The compound $[IrCl(dppm)_2]$ (50 mg, 50.2 μmol) was dissolved in 5 mL of THF, and 1 equiv (44 mg, 50.2 μmol) of $[PPN][Re(CO)_5]$ in 5 mL of THF was added via cannula. The light orange solution was then stirred for 22 h, during which time a white precipitate of PPNCl appeared. A 10-mL volume of Et_2O was then added by syringe, and the solution was filtered to remove PPNCl. After the solvent was removed in vacuo, 2 mL of CH_2Cl_2

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Table I. Spectral Data[a]

		NMR	
	IR, cm^{-1} [b]	$\delta(^{31}P\{^1H\})$ [c]	$\delta(^1H)$ [d]
$[IrRe(CO)_5(dppm)_2]$ (3)	2008 (w), 1965 (s), 1918 (s), 1905 (s), 1877 (m)	−10.1 (m), −2.8 (m)	4.71 (s, 4 H)
$[RhMn(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (4)	1977 (m), 1922 (m), 1843 (s), 1649 (m)	57.2 (m), 23.0 (dm, $^1J_{Rh-P}$ = 132 Hz)	3.38 (m, 2 H), 3.53 (m, 2 H)
$[RhRe(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (5)	1968 (s), 1905 (s), 1825 (vs), 1671 (m)	21.8 (dm, $^1J_{Rh-P}$ = 128 Hz), 16.3 (m)	3.42 (m, 2 H), 3.68 (m, 2 H)
$[IrRe(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (6)	1951 (s), 1906 (vs), 1824 (vs), 1670 (w)	14.3 (m), 14.9 (m)	4.26 (m, 2 H), 3.32 (m, 2 H)

[a] Abbreviations used: IR, w = weak, m = medium, s = strong, vs = very strong; NMR, m = multiplet, dm = doublet of multiplets, s = singlet. [b] CH_2Cl_2 cast on KBr disk. [c] Vs 85% H_3PO_4; −40 °C in CD_2Cl_2 solvent. [d] Vs TMS; 25 °C in CD_2Cl_2 solvent.

was added and CO was passed through the solution at a rate of ca. 1 mL s^{-1} for 15 min with stirring. A 20-mL volume of hexane was added, and the solution was stirred while a yellow precipitate quickly formed. The solution was filtered and the product washed with 5 × 5 mL of Et_2O. Yield: 53 mg (81%) of a bright yellow powder. Anal. Calcd for $C_{55}H_{44}IrO_5P_4Re$: C, 51.32; H, 3.44. Found: C, 51.73; H, 4.01.

(b) $[RhMn(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (4). The compound $[RhMn(CO)_4(dppm)_2]$ (1) (50 mg, 48.1 μmol) was dissolved in 10 mL of THF. A 5-mL amount (ca. 5 equiv) of O_2 was added by gastight syringe, and the yellow solution was stirred for 3 h, during which time the solution gradually turned light yellow-brown. The THF was removed in vacuo, and the residue was recrystallized from CH_2Cl_2/Et_2O to yield 43 mg (83%) of a light yellow-brown powder. Anal. Calcd for $C_{54}H_{44}MnO_6P_4Rh$: C, 60.58; H, 4.14. Found: C, 60.07; H, 4.28.

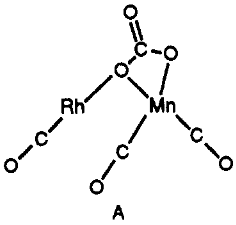
(c) $[RhRe(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (5). In a procedure identical with that of part b, 50 mg (42.8 μmol) of $[RhRe(CO)_4(dppm)_2]$ (2) was reacted with O_2 (ca. 5 equiv) over $1^1/_4$ h to yield 41 mg (80%) of a fine yellow-orange powder. Anal. Calcd for $C_{54}H_{44}O_6P_4ReRh$: C, 53.96; H, 3.69. Found: C, 53.52; H, 3.95.

(d) $[IrRe(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (6). Compound 3 (50 mg, 39 μmol) was dissolved in 5 mL of CH_2Cl_2, and 5 mL of O_2 (ca. 4 equiv) was added by syringe, causing the yellow solution to darken slightly. After 30 min of stirring, the solvent was removed in vacuo and the residue was recrystallized from CH_2Cl_2/Et_2O to yield 43 mg (85%) of an orange powder. Anal. Calcd for $C_{54}H_{44}IrO_6P_4Re$: C, 50.24; H, 3.43. Found: C, 50.88; H, 4.01.

X-ray Data Collection. Orange crystals of $[RhMn(CO)_3(\mu\text{-}CO_3)(dppm)_2]$ (4) were obtained from CH_2Cl_2/Et_2O. Suitable crystals were mounted and flame-sealed in glass capillaries under argon to minimize decomposition. Unit cell parameters were obtained from least-squares refinements of 25 well-distributed reflections in the range $20.0 \leq 2\theta \leq 24.0°$. A monoclinic cell was established by the usual peak-search and reflection indexing programs; the systematic absences established the space group as either *Cc* or *C*2/*c*. The centrosymmetric space group was established by successful refinement of the structure.

Intensity data were collected at 22 °C with use of the $\theta/2\theta$ scan technique to a maximum of $2\theta = 50.0°$. Backgrounds were scanned for 25% of the peak widths on either side of the scans. Three reflections were chosen as intensity standards and remeasured at 120-min intervals of X-ray exposure. There was no systematic decrease in the intensities, so no correction was applied. Data were processed in the usual way with a value of 0.04 for *p*,[21] and absorption corrections were applied to the data by using the method of Walker and Stuart.[22,23]

Structure Solution. The structure was solved by conventional Patterson and Fourier techniques in space group *C*2/*c*. Although location of all atoms was straightforward, initial refinements resulted in unusually high thermal parameters for several of the atoms of the carbonate and carbonyl groups. In addition the isotropic thermal parameter for Rh was unusually high (ca. 4.5 $Å^2$) while that of Mn was unusually low (ca. 0.7 $Å^2$). A difference Fourier calculation at this stage showed the presence of additional peaks corresponding to atoms of superimposed carbonyl and carbonate groups. This together with the anomalous thermal parameters for the metals led to the model shown in which two complex molecules A and B are disordered in approximately a 70:30 ratio (determined from the relative peak intensities of the ordered and disordered atoms). The two disordered molecules (A and B) are superimposed such that they have several of the atom positions in common. This is shown in C, in which Rm and Mr indicate the disordered Rh and Mn positions with Rm being 70% Rh and Mr being 70% Mn. The solid lines connect atoms of the major rotomer whereas the dashed lines show the minor one. The disordered atoms are either unprimed or primed, with the former having the higher occupancy. There was no apparent disorder involving the phosphine groups, which appeared to be well behaved.



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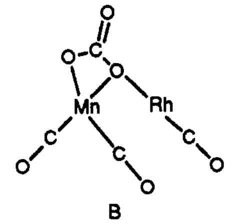

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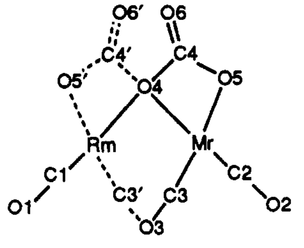

C

All non-hydrogen atoms were located. Atomic scattering factors[24,25] and anomalous dispersion terms[26] were taken from the usual sources. Hydrogen atoms were included as fixed contributions and were not refined. Their idealized positions were calculated from the geometries of the attached carbon atoms with a C–H distance of 0.95 Å being used. Hydrogens were assigned thermal parameters of 20% greater than the isotropic *B*'s of the attached carbon atoms. A summary of the crystallographic data is given in Table II. The positional and isotropic thermal parameters for the non-hydrogen atoms, except for those of the phenyl rings, are given in Table III.

Results and Discussion

The rhodium complexes of interest, $[RhM(CO)_4(dppm)_2]$ (M = Mn (1), Re (2)), are readily prepared, as previously described,[18] by reaction of $[RhCl(dppm)_2]$ with the sodium salts of the appropriate metal carbonylate anions, $M(CO)_5^-$. However, the IrRe analogue is not obtained by the analogous route utilizing $[IrCl(dppm)_2]$ and $NaRe(CO)_5$, even after 3 days in THF. On the assumption that ion pairing

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Table II. Crystal Data and Details of Intensity Collection for Compound 4

formula	$C_{54}H_{44}O_6P_4MnRh$
fw	1043.69
cell params	
a, Å	35.591 (6)
b, Å	12.556 (3)
c, Å	25.277 (5)
β, deg	116.46 (2)
V, Å^3	10112.8
space group	*C*2/*c*
Z	8
ρ(calcd), g cm^{-3}	1.371
temp, °C	22
radiation (λ, Å)	graphite-monochromated Mo K*α* (0.71069)
scan type	*θ*/2*θ*
receiving apparature, mm	2.00 (1.00 tan *θ*) wide × 4.00 high
scan speed, deg min^{-1}	1.11–6.67 (variable)
no. of unique data collcd	9278
2*θ*(max), deg	50.0
no. of unique observns	2942
cryst shape	monoclinic prism
abs coeff, cm^{-1}	7.285
transm coeff	0.901–1.113
final no. of params	366
error in observn of unit weight	2.577
R^a	0.079
R$_w$^{b}	0.104

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

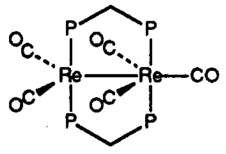
Table III. Positional Parameters and Isotropic Thermal Parameters

atom^a	*x*	*y*	*z*	*B*, Å$^{2\,b}$
Rh	−0.11852 (5)	0.1774 (2)	0.04260 (8)	3.27 (4)
Mn	−0.18187 (7)	0.0704 (2)	−0.08672 (9)	2.52 (5)
P(1)	−0.1037 (1)	0.0098 (4)	0.0831 (2)	2.7 (1)
P(2)	−0.1582 (1)	−0.0949 (4)	−0.0409 (2)	2.7 (1)
P(3)	−0.1409 (2)	0.3413 (4)	−0.0038 (2)	3.2 (1)
P(4)	−0.2072 (2)	0.2373 (5)	−0.1213 (2)	3.0 (1)
O(1)	−0.0344 (4)	0.253 (1)	0.1155 (6)	6.1 (5)
O(2)	−0.1961 (4)	0.003 (1)	−0.2056 (5)	5.4 (4)
O(3)	−0.0899 (4)	0.121 (1)	−0.0644 (6)	7.1 (4)
O(4)	−0.1774 (3)	0.123 (1)	−0.0076 (4)	2.9 (3)
O(5)	−0.2316 (4)	0.037 (1)	−0.0701 (6)	3.4 (4)
O(5)′	−0.155 (1)	0.202 (3)	0.078 (2)	1.2 (9)*
O(6)	−0.2279 (4)	0.085 (2)	0.0199 (6)	4.5 (5)
O(6)′	−0.222 (3)	0.178 (8)	0.028 (4)	14 (3)*
C(1)	−0.0660 (6)	0.224 (2)	0.0893 (9)	5.0 (7)
C(2)	−0.1920 (5)	0.027 (2)	−0.1602 (8)	3.3 (5)
C(3)	−0.1273 (8)	0.108 (2)	−0.075 (1)	5.2 (8)*
C(3)′	−0.092 (2)	0.147 (6)	−0.008 (3)	3 (2)*
C(4)	−0.2154 (8)	0.082 (2)	−0.015 (1)	4.6 (9)
C(4)′	−0.185 (2)	0.158 (6)	0.039 (3)	3 (2)*
C(5)	−0.1433 (5)	−0.092 (1)	0.0401 (6)	2.4 (5)
C(6)	−0.1952 (5)	0.333 (2)	−0.0598 (7)	3.5 (5)

^{a} Phenyl carbon parameters are given as supplementary material. ^{b} Starred *B* values are for atoms refined isotropically. *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

in the sodium salt was reducing the nucleophilicity of the $Re(CO)_5^-$ anion,[27] the PPN salt (PPN = $Ph_2PNPPh_2^+$) was used instead, resulting in the formation of two dppm-bridged IrRe products in an approximately 2:3 mole ratio within 22 h. Treatment of this solution with CO results in complete conversion of the minor product into the major one. It appears that the 1 equiv of CO released when the dppm groups unwind to bridge the two metals is readily scavenged by the resulting tetracarbonyl complex to yield the pentacarbonyl product $[IrRe(CO)_5(dppm)_2]$ (**3**). The tetracarbonyl species, $[IrRe(CO)_4(dppm)_2]$, which corresponds to the Rh complexes **1** and **2**, is not easily prepared from **3** via carbonyl loss; however, it can be prepared by another route.[28] In any case, compound **3** reacts with substrate molecules much as does the tetracarbonyl precursor and because it is more readily handled it has been used in the chemistry reported herein.

The $^{31}P\{^1H\}$ NMR spectrum of **3** displays two multiplets at δ −10.1 and −2.8. On the basis of comparison with the spectrum of the Rh analogue,[17] which displays the Re-bound phosphorus resonance at δ −1.6, the low-field resonance in **3** is assigned to the Re-bound phosphorus nuclei and the high-field resonance is assigned to those bound to Ir. The IR spectrum of **3** displays five carbonyl stretches at 2008, 1965, 1918, 1905, and 1877 cm^{-1}, again closely comparable to the Rh analogue. On the basis of these data, the structure of **3** is proposed to be analogous to that of the isoelectronic species $[RhRe(CO)_5(dppm)_2]$[17] and $[IrOs(CO)_5(dppm)_2]^+$,[19] the latter of which was characterized by an X-ray structure determination.



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The reaction of compounds **1**–**3** with O_2 in THF results in the formation of one product in each case, although at very different rates. With the RhMn compound (**1**) the reaction requires approximately 3 h, whereas the reactions with the RhRe (**2**) and IrRe (**3**) compounds are much faster, requiring only $^1/_4$ and $^1/_2$ h, respectively.

The $^{31}P\{^1H\}$ NMR spectrum of the RhMn product (**4**) displays two signals at δ 57.2 (multiplet) and 23.0 (doublet of multiplets, $^1J_{P-Rh}$ = 132 Hz) in a pattern typical of an AA′BB′X spin system, suggesting that the phosphines have remained mutually trans about each metal. The IR spectrum of **4** shows three carbonyl bands at 1977, 1922, and 1843 cm^{-1} and a band at 1649 cm^{-1}, which can be assigned as a carbonate stretch. This carbonate stretch is somewhat higher than those reported for the related carbonate-bridged dirhodium compounds, $[Rh_2(\mu\text{-}CO_3)(CO)_2(P(i\text{-}Pr)_3)_4]$[29] (1533 cm^{-1}), $[Rh_2(\mu\text{-}CO_3)(PPh_3)_5]$[30] (1485 cm^{-1}), and $[(COD)_2Rh_2(\mu\text{-}CO_3)]_3$[31] (1530 cm^{-1}); however, it is still close to the expected region for bridging carbonate complexes.[32] The ^1H NMR spectrum of **4** displays two distinct resonances for the dppm methylene protons, indicating the two faces of the complex on either side of the $RhMnP_4$ plane have different environments. It was originally suspected that water might be involved in the reactions; however, this was dismissed owing to the failure of compounds **1**–**3** to react with H_2O at ambient temperature. A search of the ^1H NMR spectra of all products

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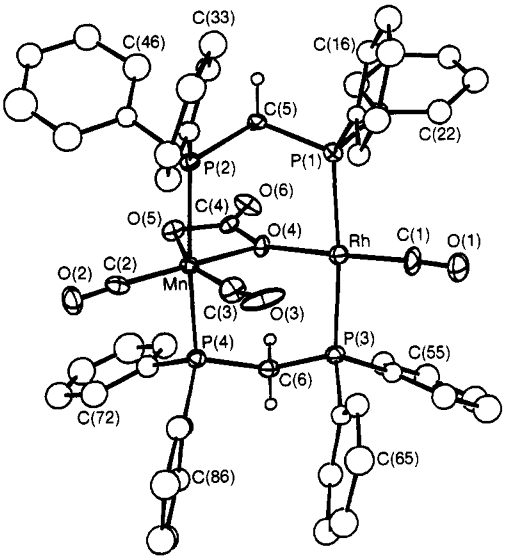

Figure 1. Perspective view of [RhMn(CO)$_3$(μ-CO$_3$)(dppm)$_2$] (4). Thermal ellipsoids are shown at the 20% level except for methylene hydrogens, which are shown arbitrarily small; phenyl hydrogens are omitted. Only one of the two disordered molecules (having the 70% occupancy) is shown.

Table IV. Selected Bond Lengths (Å) for Compound 4[a]

Rh–P(1)[b]	2.296 (4)	P(2)–C(41)	1.86 (1)
Rh–P(3)	2.327 (4)	P(3)–C(6)	1.82 (1)
Rh–O(4)	2.025 (8)	P(3)–C(51)	1.84 (1)
Rh–C(1)	1.81 (1)	P(3)–C(61)	1.79 (1)
Mn–P(2)	2.343 (4)	P(4)–C(6)	1.86 (1)
Mn–P(4)	2.295 (4)	P(4)–C(71)	1.86 (1)
Mn–O(4)	2.046 (8)	P(4)–C(81)	1.83 (1)
Mn–O(5)	2.04 (1)	C(1)–O(1)	1.09 (1)
Mn–C(2)	1.81 (2)	C(2)–O(2)	1.13 (1)
Mn–C(3)	1.89 (2)	C(3)–O(3)	1.24 (2)
Mn′–O(5)′	1.90 (2)	C(3)′–O(3)	1.51 (5)
Mn′–C(3)′	1.92 (5)	C(4)–O(4)	1.37 (2)
P(1)–C(5)	1.86 (1)	C(4)–O(5)	1.37 (2)
P(1)–C(11)	1.84 (1)	C(4)–O(6)	1.16 (2)
P(1)–C(21)	1.77 (1)	C(4)′–O(4)	1.39 (5)
P(2)–C(5)	1.87 (1)	C(4)′–O(5)′	1.22 (5)
P(2)–C(31)	1.86 (1)	C(4)′–O(6)′	1.26 (8)

[a] Additional bond lengths involving the phosphine groups are given in the supplementary material. [b] The atoms labeled Rh and Mn are actually a 70:30 mix of Rh/Mn and Mn/Rh, respectively, owing to disorder (see Experimental Section). Primed atoms have 30% occupancy and are related to the unprimed (70% occupancy) atoms by the rotational disorder.

produced no unidentified resonances; in particular no evidence of a bicarbonate proton was observed.

On the basis of these spectroscopic data, a complex containing a carbonato group and three terminal carbonyl ligands can be proposed. However, these data alone are not sufficient to establish the coordination mode of the carbonato group.

The X-ray structure determination of [RhMn(CO)$_3$(μ-CO$_3$)(dppm)$_2$] (4) confirms that the species contains a carbonate group and establishes that this group bridges the metals as shown in Figure 1. Although as noted earlier the non-phosphine components of the molecule are disordered in a 70:30 ratio, only the molecule having the larger occupancy is shown. In Tables IV and V the parameters involving both disordered molecules are shown, with the atoms of the minor species being primed; however, in this discussion only the parameters of the major species are discussed, since they are more reliable. In any case a comparison of the parameters in these tables shows excellent agreement between the two disordered molecules.

Table V. Selected Angles (deg) in Compound 4[a]

P(1)–Rh–P(3)[b]	173.9 (1)	O(4)–Mn′–O(5)′	67.6 (8)
P(1)–Rh–O(4)	86.6 (3)	O(4)–Mn′–C(3)′	101 (1)
P(1)–Rh–C(1)	92.2 (5)	O(5)′–Mn′–C(1)	111 (1)
P(3)–Rh–O(4)	87.3 (3)	O(5)′–Mn′–C(3)′	168 (2)
P(3)–Rh–C(1)	93.9 (5)	C(1)–Mn′–C(3)′	80 (2)
O(4)–Rh–C(1)	178.3 (5)	Rh–O(4)–Mn	109.2 (4)
P(2)–Mn–P(4)	172.3 (1)	Rh–O(4)–C(4)	153 (1)
P(2)–Mn–O(4)	87.2 (3)	Mn–O(4)–C(4)	95 (1)
P(2)–Mn–O(5)	82.7 (3)	Mn–O(5)–C(4)	96 (1)
P(2)–Mn–C(2)	95.8 (4)	Rh–C(1)–O(1)	177 (1)
P(2)–Mn–C(3)	91.7 (6)	Mn–C(2)–O(2)	176 (1)
P(4)–Mn–O(4)	85.5 (3)	Mn–C(3)–O(3)	172 (2)
P(4)–Mn–O(5)	91.9 (3)	O(4)–C(4)–O(5)	104 (2)
P(4)–Mn–C(2)	91.3 (4)	O(4)–C(4)–O(6)	125 (2)
P(4)–Mn–C(3)	91.7 (6)	O(5)–C(4)–O(6)	131 (2)
O(4)–Mn–O(5)	64.0 (4)	P(1)–C(5)–P(2)	115.4 (6)
O(4)–Mn–C(2)	173.6 (5)	P(3)–C(6)–P(4)	117.1 (7)
O(4)–Mn–C(3)	98.2 (7)	Mn′–O(4)–C(4)′	84 (2)
O(5)–Mn–C(2)	110.8 (5)	Rh′–O(4)–C(4)′	166 (2)
O(5)–Mn–C(3)	161.4 (7)	Mn′–O(5)′–C(4)′	95 (3)
C(2)–Mn–C(3)	87.4 (7)	Mn′–C(3)′–O(3)	157 (3)
P(1)–Mn′–O(5)′	90.3 (8)	O(4)–C(4)′–O(5)′	113 (4)
P(1)–Mn′–C(3)′	92 (2)	O(4)–C(4)′–O(6)′	117 (6)
P(3)–Mn′–O(5)′	86.9 (8)	O(5)′–C(4)′–O(6)′	124 (7)
P(3)–Mn′–C(3)′	90 (2)		

[a] Additional angles involving the phosphine groups are given in the supplementary material. [b] Labeling as in footnote *b* of Table IV.

Owing to this disorder there will be some uncertainty in the metal–ligand parameters.

Both diphosphine ligands bridge the metals in the usual trans configuration with P(1)–Rh–P(3) and P(2)–Mn–P(4) angles of 173.9 (1) and 172.3 (1)°, respectively. The metal–phosphorus distances, ranging from 2.295 (4) to 2.343 (4) Å, are normal, and as noted, any difference expected on the basis of covalent radii differences of Rh and Mn are masked by the disorder. Both metals have the geometries expected for Rh(I) and Mn(I) formulations; for Rh the geometry is almost exactly square planar whereas for Mn the slight distortion from octahedral results from the small bite of the chelating carbonate group, giving an O(4)–Mn–O(5) angle of 64.0 (4)°.

As shown in Figure 1, the carbonate dianion bridges the metals in an unusual manner. One oxygen atom (O(4)) bridges the metals, while another (O(5)) is bound solely to Mn. As such, the carbonate chelates the Mn center while simultaneously binding in a monodentate fashion to Rh. The third oxygen (O(6)) remains uncomplexed and directed away from the metals. In this binding mode the CO_3^{2-} group functions as a 6-electron donor giving Rh a 16e configuration and Mn its favored 18-valence-electron count. The carbonate coordination mode is reflected in the shorter C(4)–O(6) distance of 1.16 (2) Å for this noncoordinated oxygen atom, compared with the values involving the coordinated oxygens, for which the C(4)–O(4) and C(4)–O(5) distances both equal 1.37 (2) Å; both values are close to the values expected for double and single C–O bonds, respectively.[32] This observed bridging mode for the carbonate group in compound 4 is highly unusual. In other compounds containing bridging carbonate ligands either this group binds through all three oxygen atoms[30–32,34–38]

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or only two oxygens are bound, such that each oxygen binds to only one metal, functioning as a 2-electron donor to each.[39-43]. The observed mode is necessary in order to yield the appropriate electron counts at the metals; the mode in which all three oxygens are bound, which would also give the correct electron counts, appears not to be possible in this case, since the large separation necessary is not permitted by the bridging dppm groups. As it is, the intraligand P–P separations of 3.146 (5) and 3.137 (5) Å are large and the P-C-P angles at the methylene groups are also quite large (115.4 (6), 117.1 (7)°), showing the strain within the dppm groups. All angles around C(4) are consistent with sp^2 hybridization of this atom, apart from the slight compression of O(4)–C(4)–O(5) to 104 (2)°, resulting from chelation to Mn. For the same reason the Mn–O(4)–C(4) and Mn–O(5)–C(4) angles (95 (1) and 96 (1)°) are also somewhat compressed. All parameters within this carbonate group are consistent with other determinations involving such groups.[29-32,34-43]

The Rh–O(4), Mn–O(4), and Mn–O(5) distances (2.025 (8), 2.046 (8), 2.04 (1) Å, respectively) appear to be normal for such bonds, falling within the range (2.061 (5)–2.141 (4) Å)[30,31] observed in related carbonate-bridged dirhodium complexes and well within the rather wide range (1.88 (5)–2.32 (11) Å) noted in other carbonate-bridged species.[32] The wide Rh–O(4)–Mn angle of 109.2 (4)° and the long Rh–Mn separation of 3.317 (2) Å are consistent with the absence of a Rh–Mn bond, as expected for a Rh(I)/Mn(I) system. All atoms within the $Mn(CO_3)$ group are planar (the largest deviation being 0.03 (2) Å) although the Rh atom is situated 0.295 (2) Å out of this plane.

The spectroscopic data for compounds **5** and **6** compare closely to that of **4**. Each complex displays two resonances in the $^{31}P\{^1H\}$ NMR spectrum, and for **5** the resonance for the Rh-bound phosphorus nuclei appears close to that in **4**. However in compound **6** both sets of phosphorus resonances (Re- and Ir-bound) are at similar shifts so their differentiation is not possible, although both fall close to that for the Re-bound phosphorus nuclei in **5**. All three compounds also have similar ^1H NMR spectra and almost superimposable IR spectra, particularly in the carbonyl region. In addition all complexes show a carbonate stretch in the region between 1649 and 1671 cm^{-1}. For compound **5** the $^{13}C\{^1H\}$ NMR spectrum was obtained on a sample prepared from ca. 70% ^{13}CO-enriched starting material (**2**). This spectrum displays three carbonyl resonances at δ 203.3, 200.3, and 189.5. The first two are unresolved; however, the third is a doublet of triplets, displaying coupling of 77 Hz to the Rh nucleus and of 16 Hz to the two Rh-bound phosphorus nuclei; all signals integrate equally indicating that the species is a tricarbonyl, having two carbonyls on Re and one on Rh. The carbonate carbon, a singlet at δ 163.0, also integrating as one carbon, compares closely to the resonances reported for $[Rh_2(COD)_2(\mu\text{-}CO_3)]_3$[31] at δ 167 and for $[WH_2(CO_3)(PMe_3)_4]$ at δ 163.5.[44] These data indicate that compounds **5** and **6** are also carbonate-bridged species having structures analogous to that of **4**.

Attempts to observe intermediate species in the above transformations of a carbonyl ligand to a carbonate group were unsuccessful. Over the temperature range between −60 °C and 22 °C, only the starting materials and final products were ever observed when the reactions were monitored by $^{31}P\{^1H\}$ NMR spectroscopy. We had hoped to be able to observe the presumed O_2 adduct that precedes CO oxidation, but this was not possible. Although it appears that oxidation of a coordinated carbonyl is occurring, we cannot unambiguously rule out the possibility that CO dissociation follows O_2 coordination and that the coordinated peroxo group attacks the free CO; both mechanisms for carbon monoxide oxidation have been proposed.[45,46] It is also of interest to establish how the two metals are involved in the oxidation and to determine which carbonyl (bound to the group 9 (Rh, Ir) or the group 7 (Mn, Re) metal) is transformed. These questions also could not be addressed in this study owing to the extreme facility of the oxygen-transfer reaction and due to the fact that selectively ^{13}CO-labeled precursors (**1**–**3**) could not be obtained owing to facile CO exchange over both metals.[17]

Protonation of the carbonate groups in compounds **4**–**6** was investigated in attempts to effect conversion to the corresponding bicarbonate-bridged complexes. It was felt that under a CO atmosphere such species might react further liberating CO_2 and yielding hydroxide-bridged species such as $[MM'(CO)_4(\mu\text{-}OH)(dppm)_2]^+$ (M = Rh, Ir; M′ = Mn, Re). These attempts were unsuccessful in that in all cases the attempted protonation yielded a complex mixture of between 4 and 8 products, whether carried out in the presence or absence of CO. In the case of compound **4** these reactions always yielded paramagnetic species, which precluded the acquisition of a high-resolution NMR spectrum.

Conclusions

The low-valent, mixed-metal complexes $[RhM(CO)_4(dppm)_2]$ (M = Mn, Re) and $[IrRe(CO)_5(dppm)_2]$ react readily with O_2 resulting in the unusual oxidation of a coordinated carbonyl ligand to a bridging carbonate group. The resulting binding mode of the carbonate group, in which one oxygen atom bridges the metals while a second oxygen is chelated to the group 7 metal, appears to be unprecedented. Although the functions of the two metals were not established in this study, it is clear that mixed-metal complexes such as **1**–**3** have a rich potential for substrate activation; previous reports of oxidation of a coordinated carbonyl ligand in related mononuclear complexes are few.[46-48]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and The University of Alberta for support of this work and NSERC for partial support of the diffractometer and for funding for the PE 883 IR spectrometer. We also thank Mr. Li-Sheng Wang for assistance with the low-temperature $^{31}P\{^1H\}$ NMR studies.

Supplementary Material Available: Listings of the phenyl carbon parameters, hydrogen atom parameters, anisotropic thermal parameters, and additional bond lengths and angles (8 pages); a listing of the observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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