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# Net [2 + 2] Cycloaddition Reactions of the Oxo Complexes $Cp_2M{=}O$ (M = Mo, W) with Electrophilic Organic and Organometallic Substrates. Formation of Bimetallic $\mu_2$-$\eta^3$-$CO_2$ Complexes

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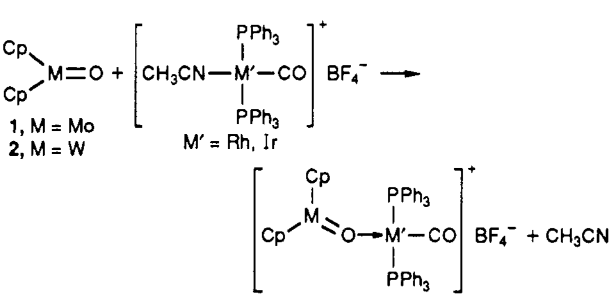
The oxo complex $Cp_2W{=}O$ (**2**) undergoes net [2 + 2] cycloaddition of the W=O bond across the C=N bonds of PhN=C=O and TolN=C=NTol and across the C=O bonds of $Ph_2C{=}C{=}O$ and $(CF_3)_2C{=}O$ to give products possessing four-membered metallacycles. A similar reaction occurs between $Cp_2Mo{=}O$ (**1**) and PhN=C=O, and crystallographic characterization of the product has shown it to possess a nearly planar Mo–N–C(O)–O ring that is perpendicular to the plane defined by the molybdenum atom and the centers of the cyclopentadienyl rings ($P2_1/c$, $a$ = 13.534 (2) Å, $b$ = 7.4063 (8) Å, $c$ = 14.448 (3) Å, $\beta$ = 99.955 (9)°, $Z$ = 4, $R(F)$ = 5.47%, $R(F)$ = 5.79% for 3097 reflections with $F_o \geq 5\sigma(F_o)$). Complex **2** also reacts with acetic anhydride and acetic acid to give the bis(acetate) complex $Cp_2W\{OC(O)CH_3\}_2$, with $Me_3SiCl$ to form $Cp_2WCl_2$ and $Me_3SiOSiMe_3$, and with MeOH to give $Cp_2W(OMe)_2$, which readily undergoes hydrolysis to re-form **2**. Addition of complexes **1** and **2** to the electrophilic carbonyl complexes $[(C_5H_4Me)Mn(CO)_2(NO)][BF_4]$, $[(C_5Me_5)Re(CO)_2(NO)][BF_4]$, $[CpFe(CO)_3][PF_6]$, $[(C_5Me_5)Ru(CO)_3][BF_4]$, and $[trans\text{-}PtCl(CO)(PEt_3)_2][BF_4]$ results in net [2 + 2] cycloaddition of the M=O bond across the C=O bond of the carbonyl ligands to yield bimetallic complexes possessing $\mu_2$-$\eta^3$-$CO_2$ ligands bridging between the metal atoms. Crystallographic characterization of the complex $[(C_5Me_5)(CO)(NO)Re(\mu_2\text{-}\eta^3\text{-}CO_2)WCp_2][BF_4]$ (**16**; $C2/c$, $a$ = 49.764 (5) Å, $b$ = 29.561 (5) Å, $c$ = 13.607 (2) Å, $\beta$ = 95.73 (1)°, $V$ = 19917 (5) Å$^3$, $Z$ = 32, $R(F)$ = 6.83%, $R(F)$ = 7.16% for 5297 reflections with $F_o \geq 5\sigma(F_o)$) has shown the carbon atom of the $CO_2$ moiety to be bound to rhenium via a rhenium–carbon double bond (2.04 (4) Å) and the two oxygen atoms of the $CO_2$ ligand to be coordinated to tungsten via nearly equivalent W–O single bonds. The preparation of complex **16** from $^{17}O$-enriched $Cp_2W{=}O$ gave $^{17}O$ enrichment in *both* the $CO_2$ and the CO ligands of the product due to an intramolecular exchange process, which has been studied by $^{17}O$ NMR spectroscopy.

## Introduction

The transfer of an oxygen atom from a metal to an organic molecule is a key step in many practiced and envisaged catalytic oxidation reactions,[1] but there are many aspects of this reaction step that are still poorly understood. One way to probe such reactions on a fundamental level is to study the interaction of oxo ligands on model compounds with organic substrates, either coordinated or free.[2] Some oxygen atom transfer reactions may proceed via the addition of a nucleophilic oxygen atom to an electron-deficient substrate, and we have sought to model such transformations using complexes with electron-rich oxo ligands, such as those found in $Cp_2Mo{=}O$ (**1**) and $Cp_2W{=}O$ (**2**). These complexes, which were first prepared by Green et al.,[3] are ideally suited for such studies since the oxo ligands are relatively electron rich and hence nucleophilic due to the fact that they are required to only donate two electrons to the metal to achieve an 18e count, in contrast to the many oxo complexes in which these ligands function as 4e donors.[4]

We have shown in other work that the oxo ligands of complexes **1** and **2** are sufficiently basic to coordinate to Rh(I) and Ir(I) centers to form bimetallic $\mu$-oxo complexes (eq 1).[5] Herein we demonstrate that the oxo ligands of



(1)

complexes **1** and **2** readily add to a variety of electrophilic organic and organometallic substrates. Net [2 + 2] cycloadditions of the Mo=O bonds occur across the C=N bonds of PhN=C=O and TolN=C=NTol and across the C=O bonds of $Ph_2C{=}C{=}O$ and $(CF_3)_2C{=}O$ to give complexes with four-membered metallacycles. Similar [2 + 2] cycloaddition occurs across the carbon–oxygen bonds

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[1] (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981. (b) Mimoun, H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1987; Vol. 6, p 317. (c) *The Enzymes*; Boyer, P. D., Ed.; Academic Press: New York, 1975; Vols. 11–13.

[2] (a) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339. (b) Herrmann, W. A. *J. Organomet. Chem.* **1986**, *300*, 111. (c) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (d) For a recent example of the reaction of a transient oxo complex with alkynes and nitriles see: Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 8751.

[3] Green, M. L. H.; Lynch, A. H.; Swan, M. G. *J. Chem. Soc., Dalton Trans.* **1972**, 1445.

[4] The related complex $(C_5Me_5)_2W{=}O$ has also been shown to have enhanced nucleophilic character, and a similar rationale has been given: (a) Parkin, G.; Marsh, R. E.; Schaefer, W. P.; Bercaw, J. E. *Inorg. Chem.* **1988**, *27*, 3262. (b) Parkin, G.; Bercaw, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 391. (c) Parkin, G.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 2053.

[5] Pilato, R. S.; Rubin, D.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1610.

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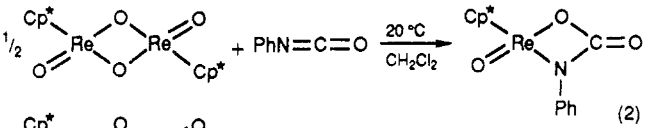
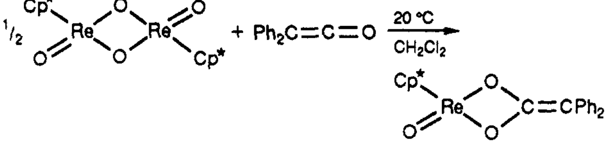
of electrophilic metal-bound carbonyl ligands to form new bimetallic complexes possessing $\mu_2$-$\eta^3$-$CO_2$ ligands that bridge between the metal atoms. Also described are reactions of complex **2** with acetic anhydride, acetic acid, $Me_3SiCl$, and MeOH. Aspects of this work have been published in preliminary communications.[6]

To put the work reported herein in perspective, it is noted that although there are many reactions that invoke the cycloaddition of organic substrates across M=O bonds,[1,2] the only previously reported examples of the formation of stable metallacycles as products from net [2 + 2] cycloaddition reactions of metal oxo complexes are those shown in eqs 2 and 3.[7]



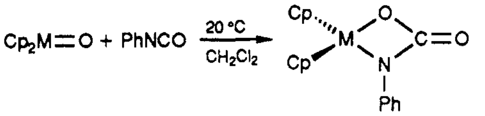
(2)



(3)

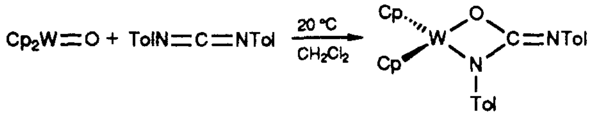
## Results and Discussion

**Cycloaddition Reactions with PhN=C=O, TolN=C=NTol, and $Ph_2C$=C=O.** Both complexes **1** and **2** readily undergo cycloaddition with PhN=C=O to give the metallacycles shown in eq 4. These reactions occur rapidly at room temperature, although an excess of the PhN=C=O reagent must be used to obtain the indicated yields. The excess PhN=C=O is converted into $[PhNCO]_x$ ($x$ = 2, 3), a reaction known to be catalyzed by Lewis bases.[8] Similar cycloaddition of $Cp_2W$=O occurs with TolN=C=NTol and $Ph_2C$=C=O to give the metallacycles shown in eqs 5 and 6. Complexes **3**–**6** were isolated as slightly air-sensitive microcrystalline solids and were spectroscopically characterized. Complex **3** was further defined by an X-ray diffraction study, the results of which are shown in Figure 1. Each of the complexes show the expected $^1H$ and $^{13}C$ NMR resonances and display parent ions in their mass spectra. Particularly characteristic of these four-membered metallacycles are the $^{13}C$ NMR resonances for the ring carbon atoms, which appear at $\delta$ 170.2 (**3**), 174.3 (**4**), 175.2 (**5**), and 181.6 (**6**) for the four compounds. An important feature in the $^{13}C$ NMR spectrum of complex **6** is a resonance at $\delta$ 46.6 attributed to the exocyclic $=CPh_2$ carbon. This resonance lies upfield of that for a typical C=C double bond, presumably due to the importance of the resonance structures



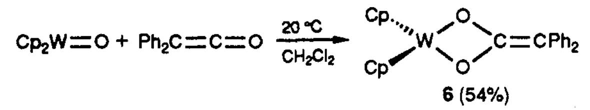
(4)

**3**, M = Mo (39%)
**4**, M = W (27%)



(5)

**5** (35%)



(6)

**6** (54%)

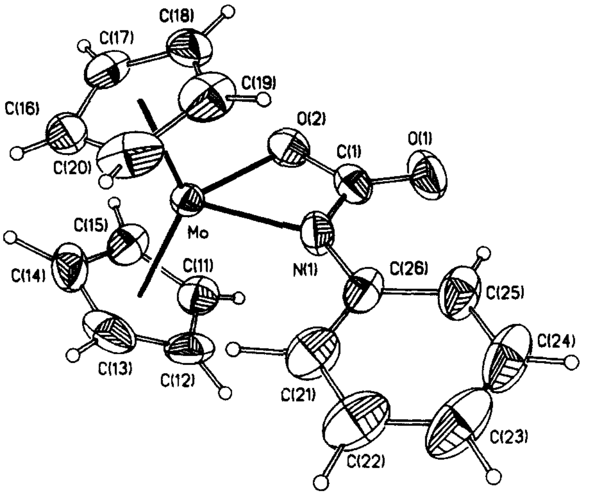
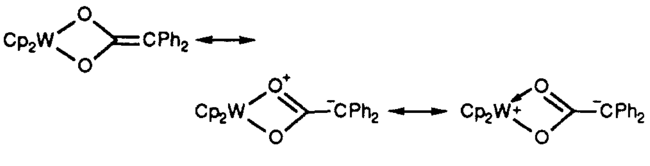


**Figure 1.** ORTEP drawing for $Cp_2Mo\{\eta^2(O,N)\text{-}OC(O)NPh\}$ (**3**).



Similar explanations have been offered to rationalize the upfield shifts of the $R_2C$=C(OR)(R) resonances of vinyl ethers,[9] and the analogous exocyclic carbon in Cp*Re(O)($O_2C$=$CPh_2$) (eq 3) has an upfield resonance at $\delta$ 67.84.[7] The lack of $^{183}W$ satellites on this resonance argues against the possibility that the W=O bond has added across the C=C bond of the $Ph_2C$=C=O substrate rather than across the C=O bond as proposed.

Imido complexes have often been prepared by the reaction of oxo complexes with isocyanates, and metallacycles similar to those in **3** and **4** are generally invoked as intermediates.[10] Thus, we attempted to convert compounds **3** and **4** into the imido derivatives of **1** and **2** by heating and by photolysis to induce $CO_2$ loss. However, no evidence for the desired imido species was obtained, and the only reaction observed was the progressive decomposition of complexes **3** and **4**.

**Crystal and Molecular Structure of $Cp_2Mo\{\eta^2(O,N)\text{-}OC(O)NPh\}$ (3).** An ORTEP drawing of complex **3** is shown in Figure 1, and the important crystallographic parameters are set out in Tables I–III. The atoms that constitute the metallacycle ring as well as the ipso carbon of the phenyl substituent on the nitrogen atom and O(1) are essentially coplanar with a maximum deviation from planarity of 0.006 (2) Å associated with N(1). This plane is nearly perpendicular (92.0 (2)°) to the plane defined by the Mo atom and the centers of the cyclopentadienyl rings.

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**Table I. Crystallographic Data for $Cp_2Mo\{\eta^2(O,N)\text{-}OC(O)NPh\}$ (3) and $[Cp^*(CO)(NO)Re{=}C(O)_2WCp_2][BF_4]$ (16)**

| | 3 | 16 |
|---|---|---|
| (a) Crystal Parameters | | |
| formula | $C_{17}H_{15}MoNO_2$ | $C_{22}H_{25}NO_4ReWBF_4$ |
| cryst syst | monoclinic | monoclinic |
| space group | $P2_1/c$ | $C2/c$ |
| $a$, Å | 13.534 (2) | 49.764 (5) |
| $b$, Å | 7.4063 (8) | 29.561 (5) |
| $c$, Å | 14.448 (3) | 13.607 (2) |
| $\beta$, deg | 99.995 (9) | 95.73 (2) |
| $V$, Å$^3$ | 1426.3 (4) | 19917 (5) |
| $Z$ | 4 | 32 |
| $d$, g/cm$^3$ | 1.680 | 2.199 |
| $T$, K | 293 | 293 |
| $T_{max}/T_{min}$ | 1.11 | 1.58 |
| (b) Data Collection | | |
| diffractometer | Nicolet R3m/$\mu$ | |
| radiation | Mo K$\alpha$ | |
| monochromator | graphite | |
| $\mu$, cm$^{-1}$ | 9.1 | 100.71 |
| scan limits, deg | 4–60 | 4–42 |
| scan method | Wyckoff | Wyckoff |
| scan speed, deg/min | 6–20 | 7–20 |
| octants collected | $\pm h,+k,+l$ | $\pm h,+k,+l$ |
| std rflns | 3 std/197 rflns | 3 std/197 rflns |
| var in stds | <1% | ~2% |
| no. of rflns collected | 4618 | 11553 |
| no. of indep rflns | 4156 | 10696 |
| no. of obs rflns | 3097 ($5\sigma(F_o)$) | 5297 ($5\sigma(F_o)$) |
| (c) Data Reduction and Refinement | | |
| $R(F)$, % | 5.47 | 6.83 |
| $R(wF)$, % | 5.79 | 7.16 |
| GOF | 1.226 | 1.193 |
| $\Delta/\sigma$ | 0.03 | 0.05 |
| $N_o/N_v$ | 12.3 | 9.13 |
| $\Delta(\rho)$, e/Å$^3$ | 1.38 | 5.0 |

**Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å$^2$ $\times$ $10^3$) for $Cp_2Mo\{\eta^2(O,N)\text{-}OC(O)NPh\}$ (3)**

| | $x$ | $y$ | $z$ | $U^a$ |
|---|---|---|---|---|
| Mo | 3322 (1) | 2093 (1) | 1460 (1) | 28 (1) |
| O(1) | 3318 (3) | −675 (6) | 3703 (2) | 56 (1) |
| O(2) | 4003 (2) | 1353 (5) | 2828 (2) | 42 (1) |
| N(1) | 2586 (3) | 186 (5) | 2180 (3) | 39 (1) |
| C(1) | 3296 (4) | 186 (7) | 2976 (3) | 39 (1) |
| C(11) | 4389 (4) | −156 (7) | 1130 (4) | 43 (2) |
| C(12) | 3490 (4) | −496 (7) | 545 (4) | 49 (2) |
| C(13) | 3255 (5) | 962 (9) | −51 (4) | 60 (2) |
| C(14) | 4055 (5) | 2211 (8) | 140 (4) | 58 (2) |
| C(15) | 4772 (4) | 1549 (7) | 905 (4) | 46 (2) |
| C(16) | 2887 (5) | 4808 (7) | 797 (4) | 52 (2) |
| C(17) | 3550 (4) | 5158 (6) | 1659 (4) | 45 (2) |
| C(18) | 3054 (4) | 4620 (7) | 2372 (4) | 46 (2) |
| C(19) | 2122 (4) | 3927 (8) | 1994 (5) | 59 (2) |
| C(20) | 1994 (4) | 3990 (8) | 1015 (5) | 60 (2) |
| C(21) | 1152 (4) | −869 (8) | 1108 (4) | 54 (2) |
| C(22) | 272 (5) | −1862 (9) | 882 (6) | 71 (3) |
| C(23) | −60 (5) | −2900 (9) | 1573 (7) | 78 (3) |
| C(24) | 472 (5) | −2901 (8) | 2447 (7) | 68 (3) |
| C(25) | 1352 (4) | −1895 (7) | 2691 (4) | 52 (2) |
| C(26) | 1707 (4) | −849 (6) | 2011 (4) | 40 (1) |

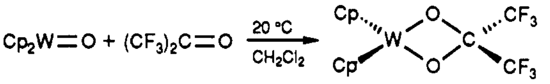
[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

The N(1)–C(1) distance (1.365 (5) Å) and the C(1)–O(2) distance (1.334 (6) Å) are indicative of partial multiple-bond character but are normal for N–C distances (1.36 (3) Å) and C–O distances (1.33 (3) Å) in structures containing the carbamate functionality.[11] The Mo–N(1) and Mo–O(2) distances appear to represent normal single bonds, and the C(1)–O(1) distance of 1.225 (6) Å is characteristic of a C=O double bond.

**Table III. Selected Bond Distances and Angles for $Cp_2Mo\{\eta^2(O,N)\text{-}OC(O)NPh\}$ (3)**

| | | | |
|---|---|---|---|
| Bond Distances (Å) | | | |
| Mo–O(2) | 2.103 (3) | C(1)–O(2) | 1.334 (6) |
| Mo–N(1) | 2.105 (4) | C(1)–O(1) | 1.225 (6) |
| C(1)–N(1) | 1.365 (5) | | |
| Bond Angles (deg) | | | |
| O(2)–Mo–N(1) | 61.9 (1) | Mo–O(2)–C(1) | 96.3 (2) |
| O(2)–C(1)–O(1) | 124.3 (4) | C(1)–N(1)–Mo | 95.2 (3) |
| O(2)–C(1)–N(1) | 106.6 (4) | C(1)–N(1)–C(26) | 126.9 (4) |
| N(1)–C(1)–O(1) | 129.1 (5) | Mo–N(1)–C(26) | 137.9 (3) |

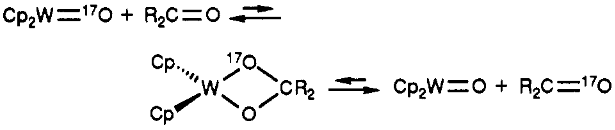
**Cycloaddition of $Cp_2W{=}O$ with Aldehydes and Ketones.** Complex 2 also undergoes net [2 + 2] cycloaddition with the highly electrophilic ketone $(CF_3)_2C{=}O$ (eq 7). The metallacyclic product 7 was isolated as a slightly air-sensitive solid and was spectroscopically characterized. It showed a parent ion in its mass spectrum at $m/z$ = 496, a single Cp $^1H$ NMR resonance at $\delta$ 5.86, and a $^{13}C$ NMR heptet at 93.14 ($J_{CF}$ = 33 Hz) for the metallacycle ring carbon, as well as Cp ($\delta$ 99.5) and $CF_3$ ($\delta$ 123.8, q, $J_{CF}$ = 145 Hz) $^{13}C$ NMR resonances.



7 (52%)

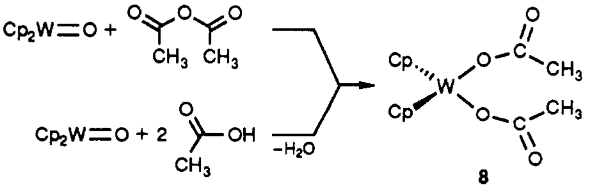
(7)

Although the reaction of other ketones and aldehydes with complex 2 failed to give evidence for the formation of stable metallacycles similar to 7, a series of experiments using partially $^{17}O$-labeled $Cp_2W{=}O$ showed that the label could be slowly transferred to benzaldehyde and acetone. Thus, when a $CH_2Cl_2$ solution containing $Cp_2W{=}^{17}O$ and benzaldehyde was stirred for 5 days, a $\delta$ 557 benzaldehyde $^{17}O$ NMR resonance appeared and slowly grew in intensity relative to that of $Cp_2W{=}O$. Similar enrichment of acetone occurred over the same 5-day period, although acetophenone was not enriched. These results may be explained by the transient formation of metallacycles analogous to 7 (eq 8), although the possibility of exchange through label equilibration with traces of water cannot be ruled out.



(8)

**Reaction of $Cp_2W{=}O$ with Acetic Anhydride, Acetic Acid, $Me_3SiCl$, and Methanol.** Complex 2 rapidly underwent reaction with acetic anhydride and with acetic acid to give in near-quantitative yields the bis(acetate) product shown in eq 9. The former reaction likely proceeds via nucleophilic addition of the oxo ligand to an electrophilic carbonyl carbon of the anhydride reagent, whereas the latter reaction probably occurs via addition of acetic acid across the W=O bond to form the hydroxy–acetate complex $Cp_2W(OH)(O_2CCH_3)$ as an intermediate. Reaction of the latter with a second equivalent



8

(9)

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[11] Values cited are mean values obtained from the Cambridge Crystallographic Database for all structures containing the carbamate moiety.

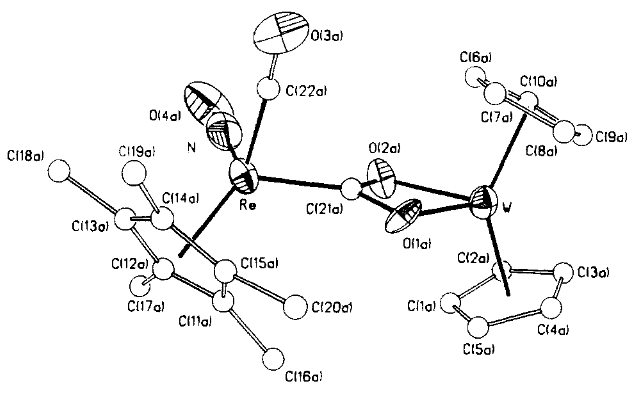
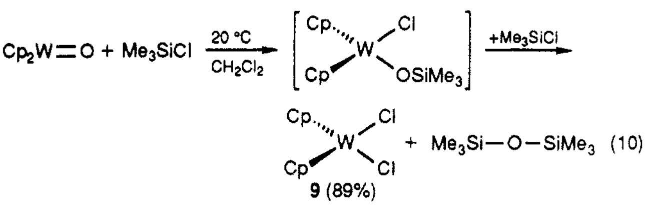


**Figure 2.** ORTEP drawing for $[Cp^*(CO)(NO)Re(\mu_2\text{-}\eta^3\text{-}CO_2)WCp_2][BF_4]$ (**16**).

of acetic acid would give compound **8** along with 1 equiv of $H_2O$. The bis(acetate) complex **8** was isolated and spectroscopically characterized. It showed a parent ion at $m/z = 432$ in its mass spectrum along with $^1H$ and $^{13}C$ NMR resonances in the expected regions (see Experimental Section).

Complex **2** also reacts with $Me_3SiCl$ to give the products shown in eq 10. $^1H$ NMR monitoring of this reaction

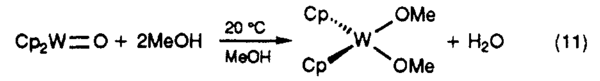


(10)

**9** (89%)

showed the initial formation of an intermediate species, which slowly disappeared as the final product **9** and $Me_3SiOSiMe_3$ ($\delta$ 0.07) formed. The 5:9 intensity ratio of the Cp and $SiMe_3$ resonances at $\delta$ 5.46 and −0.16 for this intermediate is consistent with the $Cp_2WCl(OSiMe_3)$ formulation given in eq 10. Bercaw and Parkin have demonstrated that an identical reaction occurs for the analogous $Cp^*_2W{=}O$ complex.[4c]

Dissolution of complex **2** in methanol led to the formation of the dimethoxy complex **10** (eq 11). This species

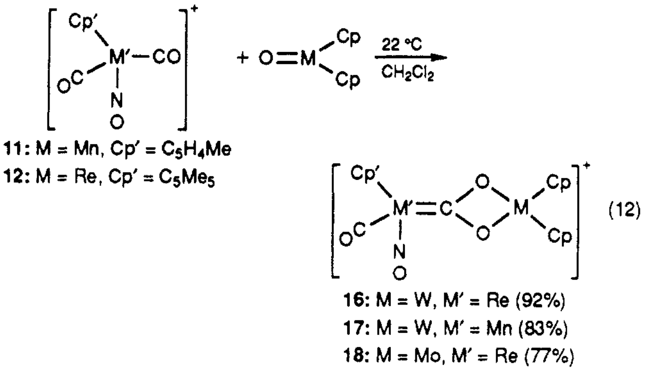


(11)

**10** (67%)

was isolated as an orange solid, but it rapidly hydrolyzed with traces of moisture to re-form complex **2** and methanol. Complex **10** was spectroscopically characterized. It showed a parent ion in its mass spectrum and Cp ($\delta$ 5.32) and $OCH_3$ ($\delta$ 3.58) resonances in the expected 5:6 intensity ratio in its $^1H$ NMR spectrum. The $^{13}C$ NMR spectrum of complex **10** showed Cp and $OCH_3$ resonances at $\delta$ 95.13 and 66.26, respectively, with the latter appearing as a quartet ($J_{CH} = 135$ Hz). This particular complex has not been reported, nor has its $C_5Me_5$ analogue. Indeed, Bercaw and Parkin showed that addition of NaOMe to $Cp^*_2WCl_2$ gave formation of the formaldehyde complex $Cp^*_2W(\eta^2\text{-}O{=}CH_2)$ and 1 equiv of methanol.[4c] We attempted to convert complex **10** into the corresponding $Cp_2W(\eta^2\text{-}O{=}CH_2)$ complex by refluxing in THF, but this gave only decomposition. No reaction occurred between excess NaOMe and **10**.

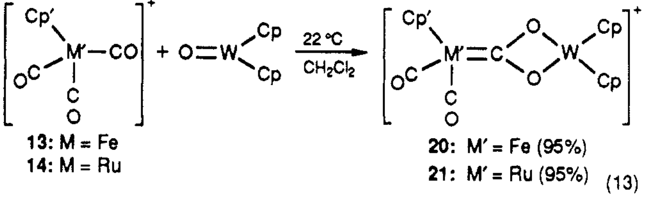
**Preparation and Spectroscopic Characterization of Bimetallic $\mu_2$-$\eta^3$-$CO_2$ Complexes.** The oxo complexes **1** and **2** rapidly react at room temperature with the cationic complexes **11**–**15** to yield the new bimetallic species **16**–**22** in good to excellent yields as air-stable microcrystalline solids (eqs 12–14). These complexes were spectroscopically characterized, with complex **16** being fully defined by an X-ray diffraction study, the results of which are shown in Figure 2. Each complex possesses a $\mu_2$-$\eta^3$-$CO_2$ ligand formed from the net [2 + 2] cycloaddition of the M═O bond across a C═O bond of the cationic carbonyl complex. Particularly diagnostic of the $CO_2$ ligands in these new complexes is the $^{13}C$ NMR resonance shown by each in the $\delta$ 243–275 region, with the exception of complex **22**, which exhibits this resonance at $\delta$ 211.8. The downfield position of these resonances emphasizes the carbene character of the $CO_2$ carbon, and they compare favorably to the corresponding $^{13}C$ NMR resonances of the dioxycarbene derivatives $[(C_5H_5)(CO)(NO)Mn{=}C(OCH_2CH_2O)][BF_4]$,[12] $[(C_5H_5)(CO)_2Fe{=}C(OCH_2CH_2O)][BF_4]$,[12] and $[(C_5H_5)(CO)_2Ru{=}C(OCH_2CH_2O)][BF_4]$,[12] which have $^{13}C$ NMR resonances for the carbene carbons at $\delta$ 263, 251, and 227, respectively.



11: M = Mn, Cp′ = $C_5H_4Me$
12: M = Re, Cp′ = $C_5Me_5$

(12)

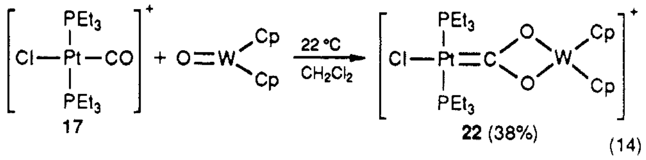
16: M = W, M′ = Re (92%)
17: M = W, M′ = Mn (83%)
18: M = Mo, M′ = Re (77%)
19: M = Mo, M′ = Mn (62%)



13: M = Fe
14: M = Ru

20: M′ = Fe (95%)
21: M′ = Ru (95%)

(13)



17

22 (38%)

(14)

It should be noted that whereas reaction 14 proceeded smoothly to give complex **22**, the corresponding reaction with $[trans\text{-}Pt(H)(PEt_3)_2(CO)][BF_4]$ did not occur. This likely reflects the differing susceptibility of the carbonyl carbon to nucleophilic attack in the two complexes, as indicated by their differing $\nu_{CO}$ stretching frequencies (X = H, $\nu_{CO} = 2050\ cm^{-1}$; X = Cl, $\nu_{CO} = 2100\ cm^{-1}$). It is well established that the higher in energy in the $\nu_{CO}$ band of a complex, the more susceptible to nucleophilic attack is the carbonyl ligand.[13]

To our knowledge, the reactions of eqs 12–14 comprise the first examples of the [2 + 2] cycloaddition of a M═O bond across a C═O bond of a carbonyl ligand. The closest related work of which we are aware is that of Collins and co-workers, who demonstrated the preparation of the Ir–Os complex **23** by the reaction shown in eq 15.[14] This reaction also involves the attack of an oxo ligand on a carbonyl

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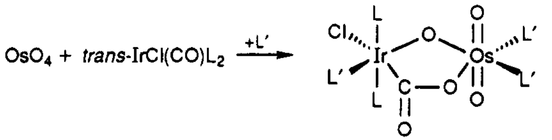
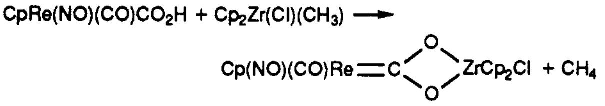


(15)

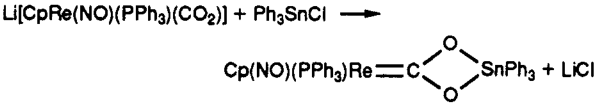
**23**: L = PPh$_3$, L' = 4-$^t$BuC$_5$H$_4$N

carbon, but the binuclear product adopts a final structure with a $CO_2$ bonding mode different from that found in the complexes **16**–**22** described above. It should also be noted that reagents such as $Me_3NO$ and PbO that are used to induce substitution reactions of metal carbonyl complexes are believed to operate by nucleophilically attacking a carbonyl carbon in a manner similar to that observed for $Cp_2Mo{=}O$ and $Cp_2W{=}O$.[15]

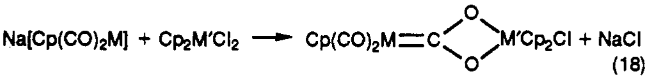
While there are no previous examples of the preparation of $\mu_2$-$\eta^3$-$CO_2$ complexes by reactions analogous to those used herein, there are several known compounds that possess $CO_2$ ligands bound in this fashion. The two most closely related to the products **16**–**22** described herein are the complexes Cp(NO)(CO)Re($\mu_2$-$\eta^3$-$CO_2$)Zr(Cl)$Cp_2$,[16a] Cp(NO)(PPh$_3$) Re($\mu_2$-$\eta^3$-$CO_2$)SnPh$_3$,[17] and the family of compounds Cp(CO)$_2$M($\mu_2$-$\eta^3$-$CO_2$)M'Cp$_2$Cl,[16b] which were prepared by the reactions shown in eqs 16–18. Similar



(16)



(17)

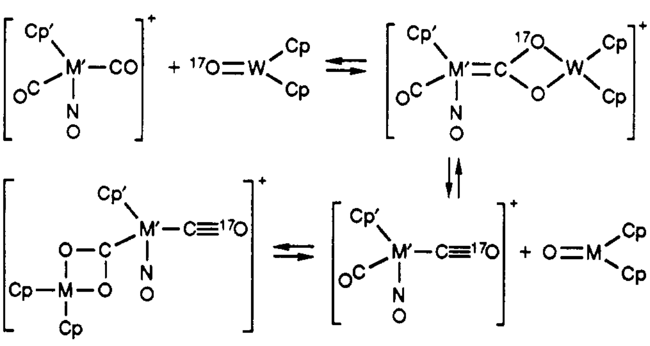


(18)

M = Fe, Ru; M' = Ti, Zr

$\mu_3$-$\eta^2$-$CO_2$ coordination has also been invoked for the salts [Cp(CO)$_2$Fe(CO$_2$)][Li][18] and [(CO)$_5$W(CO$_2$)][Na]$_2$.[19] Other related bi- and polynuclear compounds include [(CO)$_5$Re($\mu_3$-$\eta^3$-CO$_2$)Re(CO)$_4$]$_2$,[20a] [HOs$_3$(CO)$_{10}$($\mu_3$-$\eta^3$-CO$_2$)Os$_6$(CO)$_{17}$]$^-$,[20b] (C$_6$H$_5$)(Et$_3$P)$_2$Pt($\mu_2$-$\eta^2$-CO$_2$)Pt-(C$_6$H$_5$)(PEt$_3$)$_2$,[20c] (COD)$_2$Rh$_2$OsH$_2$($\mu_3$-$\eta^3$-CO$_2$)(PMe$_2$Ph)$_3$,[20d] and [Co(pr-salen)K($\mu_4$-$\eta^3$-CO$_2$)(THF)]$_n$ (pr-salen = $C_{22}H_{26}N_2O_2$).[20e]

Scheme I



**Crystallographic Characterization of [Cp*(CO)(NO)Re($\mu_2$-$\eta^3$-CO$_2$)WCp$_2$][BF$_4$] (16).** This salt crystallizes in the $C2/c$ space group with well-separated cations and anions, and the crystal lattice contains four independent but chemically similar formula units. An ORTEP drawing of one of the independent cations is shown in Figure 2, and the relevant crystallographic data are given in Tables I, IV, and V. The cation consists of a Cp*(CO)(NO)Re unit linked to a Cp$_2$W unit by the $\mu_2$-$\eta^3$-CO$_2$ ligand with the carbon bound to Re and the two oxygen atoms attached to tungsten. The structural data indicate that the CO$_2$ moiety is best viewed as a dimetalated dioxycarbene ligand with a Re=C(21) double bond (2.04 (4) Å) and with C(21)—O (average 1.33 Å) and W—O (average 2.09 Å) single bonds. The Re–C(21) distance is only slightly longer than a typical Re=C double-bond distance, as typified by Cp*(CO)$_2$Re=C(H)SiPh$_3$ (1.92 (2) Å)[21] and Cp(NO)(PPh$_3$)Re=C(H)Ph (1.949 (6) Å),[22] and compares well with the Re=C distance of 2.058 (9) Å found in the closely related compound Cp*(PPh$_3$)(NO)Re($\mu_2$-$\eta^3$-CO$_2$)-SnPh$_3$.[17]

As illustrated in Figure 2, the Re=C(O)$_2$W part of the molecule is roughly planar with a maximum deviation from planarity of 0.051 (3) Å associated with the tungsten atom. This plane is essentially perpendicular to the plane formed by the tungsten atom and the centers of the two cyclopentadienyl ligands (88.1 (2)°), and it is aligned with the Re–N–O axis and bisects the Cp*(Cnt)–Re–C(22) angle so as to maximize the Re–C(21) $\pi$-bonding.

**$^{17}$O NMR Studies.** Complexes **16** and **20** were examined by $^{17}$O NMR spectroscopy with use of samples prepared from $^{17}$O-enriched Cp$_2$W=O. The surprising result was the observation of approximately equal-intensity resonances for both the CO$_2$ and the CO ligands of the complexes, although a resonance was not observed for the nitrosyl ligands. The broad upfield resonances (**16**, $\delta$ 143; **20**, $\delta$ 168) were assigned to the CO$_2$ ligands, and the sharp downfield resonances (**16**, $\delta$ 394; **20**, $\delta$ 369) were attributed to the CO ligands on the basis of the $\delta$ 394 resonance observed in a separate experiment for [Cp*Re(CO)$_2$(NO)]$^+$. The observation of resonances for both the CO and CO$_2$ ligands implies that an exchange process occurs in these complexes that incorporates $^{17}$O into the CO ligand from the initially enriched Cp$_2$W=O reagent. One possible exchange path would involve dissociation of the Cp$_2$W=O fragment from the initially formed binuclear complex followed by readdition of Cp$_2$W=O to the "other" carbonyl

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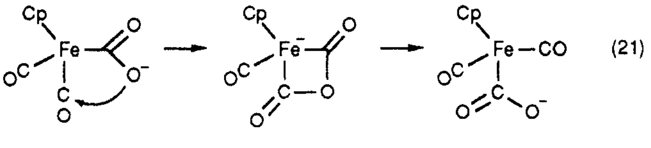
ligand (Scheme I). To test this hypothesis, the exchange reactions shown in eqs 19 and 20 were attempted. However, no exchange of the $Cp_2M{=}O$ moiety occurred when the equilibria were approached from either direction with use of a 10-fold excess of the mononuclear reagent over a 5-day period, indicating that free $Cp_2W{=}O$ is not released from the binuclear complexes. Furthermore, the reagents $PhN{=}C{=}O$ and $Me_3SiCl$, which were shown above to rapidly react with free $Cp_2M{=}O$, did not react when added to complex **18**, again indicating that formation of the binuclear $\mu_2$-$\eta^3$-$CO_2$ complexes is irreversible and that free $Cp_2M{=}O$ is not released into solution. However, these exchange studies do not preclude dissociation of $Cp_2M{=}O$ within a solvent cage.

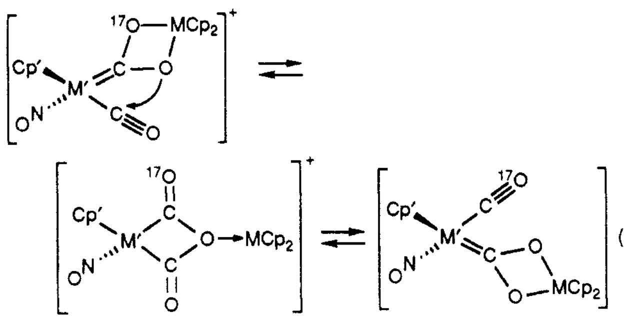
$$\mathrm{[Cp^*(CO)(NO)Re{=}CO_2WCp_2]^+ + [Cp'Mn(CO)_2(NO)]^+ \;\not\rightleftarrows\; [Cp'(CO)(NO)Mn{=}CO_2WCp_2]^+ + [Cp^*Re(CO)_2(NO)]^+} \quad (19)$$

$$\mathrm{[Cp^*(CO)_2Ru{=}CO_2WCp_2]^+ + [CpFe(CO)_3]^+ \;\not\rightleftarrows\; [Cp(CO)_2Fe{=}CO_2WCp_2]^+ + [Cp^*Ru(CO)_3]^+} \quad (20)$$

We propose a mechanism for $^{17}O$ enrichment of the CO ligands in **16** and **20** that is related to the mechanism previously suggested for oxygen atom exchange between CO and $CO_2$ ligands in $[CpFe(CO)_2(CO_2)]^-$, which invoked the intermediacy of a metalla anhydride complex (eq 21).[18b]


(21)

A similar intermediate (eq 22, **24**) could account for the observed $^{17}O$ enrichment of the CO ligands in **16** and **20**.


(22)

**24**

## Concluding Remarks

The work described herein has demonstrated the enhanced nucleophilicity of the oxo ligands in the complexes $Cp_2Mo{=}O$ and $Cp_2W{=}O$ and their ability to undergo net [2 + 2] cycloaddition reactions with both organic and organometallic substrates to yield stable metallacycles. All of these reactions likely proceed in a stepwise, rather than concerted, manner by initial oxygen atom attack on the electrophilic carbon atoms of the various substrates, followed by ring closure. To our knowledge, the only precedent for these cycloadditions are Herrmann's reactions given in eqs 2 and 3 and the related work of Collins summarized in eq 15,[7,14] although metallacycles such as these have often been invoked as intermediates in reactions involving oxo complexes.[2] Given the stability of the metallacycles described herein, it should prove possible to prepare many such derivatives by careful selection of the initial oxo complex. Such studies are currently in progress.

## Experimental Section

**General Considerations.** Diphenylketene[23] and the complexes $[Cp^*Re(CO)_2(NO)][BF_4]$,[24] $[Cp'Mn(CO)_2(NO)][BF_4]$,[25] $[CpFe(CO)_3][PF_6]$,[26] $[Cp^*Ru(CO)_3][BF_4]$,[27] [*trans*-$PtCl(PEt_3)_2(CO)$]$[BF_4]$,[28] $Cp_2Mo{=}O$,[3] and $Cp_2W{=}O$[3] were prepared according to literature procedures. The reagents $PhN{=}C{=}O$ (Aldrich), $TolN{=}C{=}NTol$ (Aldrich), and $(CF_3)_2C{=}O$ (Matheson) were obtained from commercial sources and used as received. Other solvents and reagents were dried by distillation from $CaH_2$ ($CH_2Cl_2$, pentane), $K_2CO_3$ (acetone), or $CaCl_2$ (benzaldehyde). All reactions were conducted under a prepurified $N_2$ atmosphere with use of standard Schlenk techniques. IR spectra were recorded on an IBM FTIR-32 spectrometer operated in the absorbance mode, and NMR spectra were recorded on a Bruker AM 300 FT NMR spectrometer. Field-desorption (FD) mass spectra were obtained by G. Steinmetz and R. J. Hale at the Tennessee Eastman Co., Kingsport, TN. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded on AEI-MS9 and AFAB-MS9 mass spectrometers, respectively. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories (SML), Woodside, NY, and Galbraith Laboratories (GL), Knoxville, TN.

**Preparation of $^{17}$O-Enriched $Cp_2W{=}O$.** A $CH_2Cl_2$ (50 mL) solution of $Cp_2W{=}O$ (200 mg, 0.608 mmol) and 100 μL of 17% $^{17}O$-enriched $H_2O$ (Cambridge Isotopes) was stirred for 12 h. The solution was dried over $MgSO_4$ and filtered, and the solvent was removed under vacuum. $^{17}O$ NMR (20% $CD_2Cl_2$/80% $CH_2Cl_2$): $\delta$ 775 (fwhm = 50 Hz). All $^{17}O$ NMR studies were conducted with complexes prepared from this reagent.

**Preparation of $Cp_2Mo\{\eta^2(O,N)$-OC(O)NPh\} (3).** To a $CH_2Cl_2$ (20 mL) solution of $Cp_2Mo{=}O$ (250 mg, 1.07 mmol) was added dropwise PhNCO (1.0 mL, 1.07 g, 9.2 mmol). The reaction mixture was stirred at room temperature for 1.5 h as the color changed from green to red. Removal of the solvent under reduced pressure followed by trituration with pentane (2 × 30 mL) left complex **3** as a tan powder contaminated with significant quantities of a mixture of $[PhNCO]_x$ ($x = 2, 3$). This solid mixture was dissolved in $CH_2Cl_2$ (20 mL), and the solution was filtered through a pad of Celite. The volume was reduced to 5 mL, and $Et_2O$ (50 mL) was added to precipitate the crude product. Further repetitive recrystallization from 1:10 $CH_2Cl_2/Et_2O$ gave analytically pure **3** as an orange microcrystalline solid in 39% yield (150 mg, 0.48 mmol). Anal. (GL) Calcd for $C_{17}H_{15}O_2Mo$: C, 56.52; H, 4.19; N, 3.95. Found: C, 56.20; H, 4.42; N, 3.95. IR (KBr): 3110 (w), 3090 (w), 1626 (vs), 1588 (m), 1485 (s), 1449 (m), 1428 (m), 1372 (w), 1335 (vs), 1285 (m), 1225 (s), 1076 (m), 1018 (m) $cm^{-1}$. $^1H$ NMR (acetone-$d_6$): $\delta$ 7.35–6.65 (m, Ph, 5 H), 5.58 (s, Cp, 10 H). $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 170.2 (CO), 148.9, 128.6, 121.2, 119.9 (Ph), 99.0 (Cp).

**Preparation of $Cp_2W\{\eta^2(O,N)$-OC(O)NPh\} (4).** Complex **4** was prepared as above for complex **3** with $Cp_2W{=}O$ (500 mg, 1.52 mmol) and PhNCO (1.5 mL, 1.64 g, 13.7 mmol) and was obtained as an orange microcrystalline solid in 27% yield (185 mg, 0.412 mmol). Anal. (GL) Calcd for $C_{17}H_{15}O_2W$: C, 45.45; H, 3.37. Found: C, 45.05; H, 3.41. IR (KBr): 3099 (w), 2919 (w), 1640 (vs), 1592 (m), 1485 (s), 1322 (s), 1222 (m), 1078 (w), 1018 (w) $cm^{-1}$. $^1H$ NMR (acetone-$d_6$): $\delta$ 7.46–6.72 (m, Ph, 5 H), 5.56 (s, Cp, 10 H). $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 174.3 (CO), 148.3, 128.7, 121.9, 120.4 (Ph), 94.3 (Cp). MS (EI): $m/z$ = 448 ($M^+$).

**Preparation of $Cp_2W\{\eta^2(O,N)$-OC(=NTol)NTol\} (5).** The complex $Cp_2W{=}O$ (200 mg, 0.455 mmol) and $TolN{=}C{=}NTol$ (100 mg, 0.455 mmol) were dissolved in $CH_2Cl_2$ (1 mL) and the solution was allowed to stand for 3 days without stirring. The orange crystals of **5** that precipitated were isolated by decanting the solvent and washing with 5 × 5 mL portions of pentane (89 mg, 0.1612 mmol, 35%). Anal. Calcd for $C_{25}H_{24}N_2OW{\cdot}CH_2Cl_2$: C, 49.00; H, 4.11. Found: C, 49.45; H, 4.09. IR (KBr): 3094 (w),

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**Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å$^2$ × $10^3$) for [$Cp^*(CO)(NO)Re(\mu_2$-$\eta^3$-$CO_2)WCp_2][BF_4]$ (16)**

| | $x$ | $y$ | $z$ | $U^a$ |
|---|---|---|---|---|
| W(a) | 4255 (1) | -1119 (1) | 166 (1) | 49 (1)* |
| Re(a) | 4435 (1) | 415 (1) | -30 (1) | 50 (1)* |
| O(1a) | 4273 (4) | -477 (8) | 823 (15) | 53 (10)* |
| O(2a) | 4342 (5) | -561 (8) | -675 (16) | 56 (10)* |
| O(3a) | 4967 (6) | 244 (11) | 1272 (22) | 102 (15)* |
| O(4a) | 4631 (7) | 423 (12) | -2043 (21) | 125 (17)* |
| N(a) | 4558 (6) | 407 (12) | -1219 (27) | 91 (16)* |
| C(1a) | 3830 (6) | -968 (9) | -640 (21) | 68 (13) |
| C(2a) | 3911 | -1404 | -933 | 78 (14) |
| C(3a) | 3934 | -1688 | -87 | 93 (16) |
| C(4a) | 3866 | -1427 | 730 | 71 (13) |
| C(5a) | 3801 | -983 | 388 | 81 (14) |
| C(6a) | 4721 (6) | -1147 (11) | 36 (24) | 87 (15) |
| C(7a) | 4687 | -1093 | 1053 | 88 (15) |
| C(8a) | 4541 | -1472 | 1358 | 86 (15) |
| C(9a) | 4485 | -1761 | 530 | 89 (15) |
| C(10a) | 4596 | -1560 | -288 | 93 (16) |
| C(11a) | 4004 (4) | 633 (8) | 185 (19) | 35 (9) |
| C(12a) | 4102 | 939 | -500 | 54 (11) |
| C(13a) | 4326 | 1173 | -12 | 64 (12) |
| C(14a) | 4366 | 1011 | 975 | 81 (14) |
| C(15a) | 4167 | 678 | 1096 | 70 (13) |
| C(16a) | 3750 (9) | 330 (16) | -22 (34) | 98 (16) |
| C(17a) | 3980 (8) | 1037 (14) | -1550 (29) | 72 (13) |
| C(18a) | 4501 (11) | 1531 (20) | -465 (41) | 134 (21) |
| C(19a) | 4567 (11) | 1204 (19) | 1851 (41) | 135 (21) |
| C(20a) | 4080 (10) | 376 (18) | 2024 (37) | 116 (18) |
| C(21a) | 4351 (7) | -259 (13) | 40 (27) | 58 (11) |
| C(22a) | 4764 (8) | 288 (15) | 717 (31) | 82 (14) |
| W(b) | 2632 (1) | 801 (1) | 4715 (1) | 56 (1)* |
| Re(b) | 2040 (1) | 1791 (1) | 6049 (1) | 58 (1)* |
| O(1b) | 2279 (5) | 1199 (10) | 4499 (17) | 76 (12)* |
| O(2b) | 2499 (6) | 1174 (11) | 5917 (17) | 94 (14)* |
| O(3b) | 2456 (7) | 2530 (13) | 6153 (28) | 147 (20)* |
| O(4b) | 2229 (7) | 1420 (15) | 8016 (25) | 149 (21)* |
| N(b) | 2167 (7) | 1589 (15) | 7292 (28) | 120 (21)* |
| C(1b) | 2718 (6) | 55 (12) | 4481 (29) | 102 (17) |
| C(2b) | 2466 | 159 | 3943 | 122 (20) |
| C(3b) | 2282 | 280 | 4632 | 111 (18) |
| C(4b) | 2420 | 251 | 5595 | 103 (17) |
| C(5b) | 2690 | 112 | 5501 | 96 (16) |
| C(6b) | 2863 (7) | 1458 (10) | 4644 (31) | 90 (15) |
| C(7b) | 3043 | 1136 | 5121 | 116 (19) |
| C(8b) | 3081 | 785 | 4435 | 127 (20) |
| C(9b) | 2924 | 891 | 3534 | 124 (19) |
| C(10b) | 2789 | 1307 | 3664 | 145 (23) |
| C(11b) | 1691 (6) | 2192 (7) | 5235 (21) | 77 (14) |
| C(12b) | 1616 | 2090 | 6190 | 48 (10) |
| C(13b) | 1602 | 1612 | 6278 | 70 (13) |
| C(14b) | 1669 | 1419 | 5379 | 47 (10) |
| C(15b) | 1724 | 1778 | 4734 | 65 (12) |
| C(16b) | 1700 (8) | 2679 (15) | 4768 (30) | 79 (13) |
| C(17b) | 1557 (9) | 2424 (17) | 7007 (35) | 96 (16) |
| C(18b) | 1524 (9) | 1369 (15) | 7134 (32) | 86 (15) |
| C(19b) | 1671 (8) | 889 (15) | 5150 (30) | 78 (13) |
| C(20b) | 1757 (8) | 1740 (14) | 3631 (30) | 74 (13) |
| C(21b) | 2285 (6) | 1360 (12) | 5378 (24) | 43 (10) |
| C(22b) | 2309 (7) | 2243 (13) | 6086 (27) | 59 (11) |
| W(c) | 1781 (1) | 1411 (1) | 550 (1) | 44 (1)* |
| Re(c) | 1924 (1) | 2933 (1) | 18 (1) | 41 (1)* |
| O(1c) | 1808 (4) | 1954 (8) | -444 (16) | 53 (10)* |
| O(2c) | 1780 (5) | 2080 (7) | 1073 (16) | 53 (10)* |
| O(3c) | 2453 (5) | 2721 (10) | 1247 (25) | 103 (15)* |
| O(4c) | 2118 (7) | 2923 (12) | -1997 (23) | 112 (17)* |
| N(c) | 2058 (6) | 2871 (9) | -1171 (21) | 55 (12)* |
| C(1c) | 1328 (5) | 1469 (8) | -182 (18) | 76 (13) |
| C(2c) | 1319 | 1508 | 854 | 47 (10) |
| C(3c) | 1426 | 1104 | 1302 | 61 (12) |
| C(4c) | 1502 | 815 | 543 | 58 (11) |
| C(5c) | 1442 | 1041 | -374 | 38 (9) |
| C(6c) | 2117 (6) | 1124 (10) | 1756 (15) | 59 (11) |
| C(7c) | 2055 | 803 | 991 | 70 (13) |
| C(8c) | 2127 | 993 | 95 | 69 (13) |
| C(9c) | 2233 | 1433 | 307 | 55 (11) |
| C(10c) | 2227 | 1513 | 1333 | 81 (14) |
| C(11c) | 1498 (4) | 3138 (8) | 373 (19) | 41 (9) |
| C(12c) | 1574 | 3418 | -403 | 51 (11) |
| C(13c) | 1805 | 3670 | -35 | 71 (13) |
| C(14c) | 1872 | 3547 | 967 | 70 (13) |
| C(15c) | 1683 | 3218 | 1220 | 74 (13) |
| C(16c) | 1253 (7) | 2832 (13) | 283 (28) | 60 (12) |
| C(17c) | 1424 (9) | 3474 (16) | -1482 (34) | 96 (16) |
| C(18c) | 1955 (8) | 4012 (15) | -662 (31) | 81 (14) |
| C(19c) | 2091 (10) | 3814 (18) | 1539 (38) | 118 (19) |
| C(20c) | 1669 (9) | 3066 (15) | 2213 (33) | 88 (15) |
| C(21c) | 1810 (5) | 2268 (10) | 219 (21) | 23 (8) |
| C(22c) | 2273 (7) | 2787 (12) | 707 (26) | 53 (11) |
| W(d) | 148 (1) | 1671 (1) | 70 (2) | 90 (1)* |
| Re(d) | -526 (1) | 617 (1) | 227 (2) | 85 (1)* |
| O(1d) | -196 (5) | 1325 (9) | -597 (21) | 88 (13)* |
| O(2d) | -89 (6) | 1266 (11) | 891 (23) | 115 (16)* |
| O(3d) | -147 (10) | 60 (15) | -1053 (30) | 205 (28)* |
| O(4d) | -345 (8) | 293 (20) | 2176 (31) | 242 (32)* |
| N(d) | -382 (8) | 404 (23) | 1369 (29) | 195 (35)* |
| C(1d) | 557 (9) | 1431 (18) | 613 (26) | 161 (26) |
| C(2d) | 576 | 1663 | -291 | 105 (18) |
| C(3d) | 435 | 1407 | -1060 | 195 (31) |
| C(4d) | 328 | 1016 | -631 | 124 (21) |
| C(5d) | 404 | 1031 | 403 | 163 (26) |
| C(6d) | 102 (8) | 2405 (12) | -624 (21) | 98 (16) |
| C(7d) | -153 | 2292 | -311 | 89 (15) |
| C(8d) | -117 | 2212 | 722 | 102 (17) |
| C(9d) | 160 | 2275 | 1048 | 126 (20) |
| C(10d) | 296 | 2395 | 216 | 118 (19) |
| C(11d) | -838 (6) | 793 (11) | -1052 (18) | 84 (15) |
| C(12d) | -865 | 1117 | -298 | 85 (14) |
| C(13d) | -945 | 884 | 539 | 94 (16) |
| C(14d) | -967 | 417 | 302 | 81 (14) |
| C(15d) | -901 | 361 | -682 | 61 (12) |
| C(16d) | -768 (9) | 885 (16) | -2081 (34) | 95 (16) |
| C(17d) | -844 (7) | 1669 (14) | -424 (28) | 68 (12) |
| C(18d) | -1019 (9) | 1131 (16) | 1535 (33) | 94 (15) |
| C(19d) | -1072 (10) | 12 (19) | 934 (39) | 120 (19) |
| C(20d) | -933 (8) | -91 (152) | -1297 (31) | 80 (14) |
| C(21d) | -261 (11) | 246 (18) | -537 (39) | 124 (20) |
| C(22d) | -249 (8) | 1132 (14) | 189 (30) | 73 (13) |
| B(1) | 888 (4) | 2427 (4) | 2711 (15) | 741 (220) |
| F(1) | 1062 (6) | 2438 (10) | 3411 (21) | 269 (24) |
| F(2) | 960 (7) | 2171 (5) | 2082 (23) | 225 (19) |
| F(3) | 855 (3) | 2807 (3) | 2365 (9) | 171 (14) |
| F(4) | 677 (6) | 2289 (8) | 2992 (24) | 200 (17) |
| B(2) | 3335 (2) | 133 (6) | 7335 (7) | 636 (169) |
| F(5) | 3115 (2) | 117 (5) | 7660 (16) | 224 (19) |
| F(6) | 3484 (4) | -154 (11) | 7744 (10) | 222 (19) |
| F(7) | 3435 (5) | 508 (8) | 7487 (15) | 250 (22) |
| F(8) | 3307 (4) | 63 (4) | 6444 (6) | 215 (18) |
| B(3) | 1742 (2) | 49 (9) | 7729 (13) | 885 (273) |
| F(9) | 1732 (6) | -360 (9) | 7861 (22) | 142 (12) |
| F(10) | 1767 (7) | 251 (12) | 8518 (21) | 179 (15) |
| F(11) | 1930 (5) | 143 (13) | 7248 (23) | 191 (16) |
| F(12) | 1530 (4) | 171 (13) | 7272 (26) | 216 (18) |
| B(4) | 766 (4) | 2527 (7) | 7631 (10) | 587 (154) |
| F(13) | 833 (3) | 2647 (4) | 6831 (7) | 233 (19) |
| F(14) | 914 (7) | 2222 (11) | 7965 (20) | 221 (18) |
| F(15) | 533 (5) | 2392 (14) | 7528 (24) | 258 (22) |
| F(16) | 784 (10) | 2848 (11) | 8200 (14) | 348 (33) |

[a] Asterisks denote equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

3021 (w), 2920 (w), 2865 (w), 1612 (s), 1572 (vs), 1558 (vs), 1500 (vs), 1347 (vs), 1235 (vs), 1235 (s), 1107 (w), 1101 (m), 956 (w), 919 (w), 877 (w), 835 (w), 814 (m) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$): $\delta$, 7.46–6.74 (m, Tol, 8 H), 5.48 (s, Cp, 10 H), 2.28 (s, $CH_3$, 3 H), 2.24 (s, $CH_3$, 3 H). $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 175.2 ($C{=}N$), 146.5, 145.2, 129.8, 129.0, 128.9, 123.9, 122.3 (aryl), 95.0 (Cp), 20.8 ($CH_3$), 20.6 ($CH_3$). MS (EI): $m/z$ = 552.1406 (M$^+$); calcd for $C_{24}H_{25}N_2OW$ $m/z$ = 552.1399.

**Preparation of $Cp_2W\{\eta^2(O,O)$-$OC({=}CPh_2)O\}$ (6).** A $CH_2Cl_2$ (10 mL) solution of $Cp_2W{=}O$ (400 mg, 1.22 mmol) was filtered

**Table V. Selected Bond Distances and Angles for Molecule A of [Cp*(CO)(NO)Re($\mu_2$-$\eta^3$-CO$_2$)WCp$_2$][BF$_4$] (16)**

| | | | |
|---|---|---|---|
| (a) Bond Distances (Å) | | | |
| W(a-O(1) | 2.09 (2) | Re(a)-C(22a) | 1.88 (4) |
| W(a)-O(2) | 2.08 (2) | Re(a)-Cnt(3) | 1.95 (2) |
| W(a)-Cnt(1) | 1.99 (3) | Re(a)-C(21a) | 2.04 (4) |
| W(a)-Cnt(2) | 1.96 (3) | O(1a)-C(21a) | 1.34 (4) |
| Re(a)-N(a) | 1.79 (4) | O(22)-C(21a) | 1.32 (4) |
| (b) Bond Angles (deg) | | | |
| Cnt(1)-W-Cnt(2) | 139.0 (9) | Re(a)-C(21a)-O(1a) | 125.8 (26) |
| Cnt(3)-Re(a)-N(a) | 122 (1) | Re(a)-C(21a)-O(2a) | 128.2 (26) |
| Cnt(3)-Re(a)-C(22a) | 122 (1) | C(21a)-Re(a)-C(22a) | 80.7 (16) |
| N(a)-Re(a)-C(22a) | 97 (2) | C(21a)-Re(a)-N(a) | 96.8 (15) |
| O(2a)-C(21a)-O(1a) | 106 (3) | Re(a)-C(22a)-O(3a) | 172.3 (39) |
| O(1a)-W(a)-O(2a) | 60.9 (9) | Re(a)-N(a)-O(4a) | 176.0 (30) |
| W(a)-O(2a)-C(21a) | 97.2 (20) | N(a)-Re(a)-C(22a) | 97.4 (17) |
| W(a)-C(21a)-Re(a) | 178.4 (21) | | |

through Celite, and $Ph_2C{=}C{=}O$ (212 $\mu$L, 236 mg, 1.22 mmol) was added in a single aliquot. This included immediate precipitation of **6** as a red crystalline solid. The solution was cooled to −30 °C, and the mother liquor was removed. The red solid was washed with pentane (3 × 15 mL) and dried under vacuum to give **6** in 54% yield (390 mg, 0.589 mmol). Anal. Calcd for $C_{23}H_{20}O_2W$: C, 55.00; H, 3.82. Found: C, 54.76; H, 3.82. IR (KBr): 3125 (s), 1635 (vs), 1594 (s), 1490 (s), 1440 (s), 1240 (s), 1013 (s), 698 (s) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$): $\delta$, 7.50–7.00 (m, Ph, 10 H), 4.95 (s, Cp, 10 H). $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 181.6 ($O_2C$), 151.9, 128.0, 127.7, 124.6 (Ph), 93.2 (Cp), 46.7 ($CPh_2$). $^{17}$O NMR ($CD_2Cl_2$): $\delta$ 90.8 MS (FD): $m/z$ = 524 (M$^+$).

**Preparation of $Cp_2W\{\eta^2(O,O)\text{-}OC(CF_3)_2O\}$ (7).** A solution of $Cp_2W{=}O$ (200 mg, 0.606 mmol) in $CH_2Cl_2$ (25 mL) was filtered through Celite into a 100-mL Schlenk flask, which was then evacuated. The flask was backfilled with gaseous $(CF_3)C{=}O$, and the reaction mixture was stirred for 30 min. The solvent was reduced to 5 mL under vacuum, and pentane (50 mL) was added to induce precipitation of **7** as a gray solid, which was isolated by filtration (155 mg, 0.313 mmol, 52%).

Anal. Calcd for $C_{13}H_{10}F_6O_2W\cdot CH_2Cl_2$: C, 28.94; H, 2.08. Found: C, 28.31; H, 2.02. IR (KBr): 3133 (w), 2930 (w), 1215 (m), 1191 (vs), 1131 (s), 1099 (vs), 948 (w), 876 (w), 835 (w), 805 (w), 740 (w), 720 (w) cm$^{-1}$. $^1$H NMR (acetone-$d_6$): $\delta$ 5.86 (Cp). $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 123.8 (q, $CF_3$, $J_{CF}$ = 145 Hz), 99.5 (s, Cp), 93.14 (heptet, $C(CF_3)_2$, $J_{CF}$ = 33 Hz). MS (EI): $m/z$ = 496 (M$^+$).

**Reaction of $^{17}$O-Enriched $Cp_2W{=}O$ with Acetone, Benzaldehyde, and Acetophenone.** $^{17}$O-enriched $Cp_2W{=}O$ (33 mg, 0.10 mmol), prepared as described above, was dissolved in $CD_2Cl_2$ (0.6 mL), and 25 $\mu$L of benzaldehyde was added with a micropipet. The $^{17}$O NMR spectrum of this solution was recorded (10$^5$ scans with a left shift base line adjustment and without peak enhancement) daily for 5 days. Initially only the $\delta$ 775 resonance for $Cp_2W{=}O$ was observed. After 1 day the $^{17}$O NMR resonance for PhCHO ($\delta$ 557) began to appear and it continued to increase in intensity relative to that of $Cp_2W{=}O$ over the next 4 days. Similar experiments were conducted with acetone (25 $\mu$L) and acetophenone (30 mg). A resonance for acetone was observed at $\delta$ 569, but no resonance for acetophenone appeared during the 5-day period.

**Preparation of $Cp_2W\{OC(O)CH_3\}_2$ (8) by the Reaction of $Cp_2W{=}O$ with Acetic Anhydride.** A $CH_2Cl_2$ (15 mL) solution of $Cp_2W{=}O$ (330 mg, 1.0 mmol) was filtered through Celite, and acetic anhydride (0.5 mL, 4.9 mmol) was added dropwise. The solution was stirred for 30 min, and the solvent was removed under vacuum. The resultant solid residue was washed with pentane and recrystallized from 1:20 $CH_2Cl_2$/pentane to give **8** as a red solid in 97% yield (420 mg, 0.97 mmol).

Anal. Calcd for $C_{14}H_{16}O_4W$: C, 38.93; H, 3.70. Found: C, 39.01; H, 4.02. IR (KBr): 3476 (m), 3414 (m), 3111 (w), 1625 (vs), 1614 (vse, 1387 (s), 1370 (s), 1314 (vs) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$): $\delta$ 5.54 (s, Cp, 10 H), 1.89 (s, $CH_3$, 6 H). $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 179.63 (CO), 97.43 (Cp), 23.11 ($CH_3$). MS (EI): $m/z$ = 432 (M$^+$).

**Preparation of $Cp_2W\{OC(O)CH_3\}_2$ (8) by the Reaction of $Cp_2W{=}O$ with Acetic Acid.** A $CH_2Cl_2$ (15 mL) solution of $Cp_2W{=}O$ (330 mg, 1 mmol) was filtered through Celite, and acetic acid (0.5 mL, 8.3 mmol) was added in one aliquot. The solution was stirred for 15 min, and the solvent was removed under vacuum. The resultant solid residue was washed with pentane and left under vacuum for 12 h to remove any remaining acetic acid. Recrystallization from $CH_2Cl_2$/pentane gave **8** as a red crystalline solid in 96% yield (414 mg 0.96 mmol).

**Reaction of $Cp_2W{=}O$ with $Me_3SiCl$.** A $CD_2Cl_2$ (0.6 mL) solution of $Cp_2W{=}O$ (33 mg, 0.10 mmol) was filtered through a pad of Celite and added to a 5-mL NMR tube sealed with a septum cap in the drybox. The tube was removed from the drybox and cooled to 0 °C in an ice–water bath, and $Me_3SiCl$ (28 $\mu$L, 0.20 mmol) was added via syringe. The sample was warmed to 22 °C and monitored by $^1$H NMR spectroscopy. The spectrum taken within a few minutes after addition of $Me_3SiCl$ showed the presence of a species with Cp and $SiMe_3$ resonances at $\delta$ 5.46 and $\delta$ −0.16, respectively, but no $Cp_2W{=}O$ remained. After 1 h, green $Cp_2WCl_2$ (MS (EI): $m/z$ = 384 (M$^+$) began to precipitate, and this species was isolated in 89% yield (34 mg, 0.089 mmol) by filtering the NMR solution. The $^1$H NMR spectrum of the filtrate showed a single resonance at $\delta$ 0.07 attributed to $Me_3SiOSiMe_3$.

**Preparation of $Cp_2W(OCH_3)_2$ (10).** The complex $Cp_2W{=}O$ (330 mg, 1 mmol) was dissolved in dry, degassed MeOH (25 mL), and the solution was stirred for 30 min. The volume of MeOH was reduced to 5 mL, and $Et_2O$ (50 mL) was added to precipitate complex **10** as a red solid. This solid was recrystallized from $CH_2Cl_2$/pentane to give **10** in 67% yield (252 mg, 0.67 mmol) as a very moisture-sensitive solid that did not give satisfactory analyses. $^1$H NMR ($CD_2Cl_2$): $\delta$ 5.32 (s, Cp, 10 H), 3.58 (s, $CH_3$, 6 H). $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 95.13 (Cp), 66.26 ($CH_3$). MS (EI): $m/z$ = 376 (M$^+$).

**Preparation of [Cp*(CO)(NO)Re($\mu_2$-$\eta^3$-CO$_2$)WCp$_2$][BF$_4$] (16).** A solution of $Cp_2W{=}O$ (73 mg, 0.222 mmol) in $CH_2Cl_2$ (15 mL) was filtered through a pad of Celite and added to a $CH_2Cl_2$ (15 mL) solution of [Cp*Re(CO)$_2$(NO)][BF$_4$] (100 mg, 0.202 mmol). The solution was stirred for 15 min, and the solvent was removed under vacuum. The flask was exposed to air for 10 min to degrade any remaining $Cp_2W{=}O$. The residue was dissolved in $CH_2Cl_2$ (25 mL) and filtered through a pad of Celite, and the solvent was removed under vacuum to give **16** as a brown solid in 92% yield (153 mg, 0.186 mmol). Anal. Calcd for $C_{22}H_{25}BF_4NO_4ReW$: C, 32.06; H, 3.03. Found: C, 32.20; H, 3.17. IR ($CH_2Cl_2$): $\nu_{CO}$ = 1990 (vs) cm$^{-1}$, $\nu_{NO}$ = 1727 (vs) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$): $\delta$ 5.98 (s, $C_5H_5$, 10 H), 2.08 (s, $C_5Me_5$, 15 H). $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 247.4 (s, $CO_2$), 202.8 (s, CO), 106.1 (s, $C_5Me_5$), 98.0 (s, $C_5H_5$), 10.2 (s, $C_5Me_5$). $^{17}$O NMR (20% $CD_2Cl_2$.80% $CH_2Cl$): $\delta$ 394 (s, CO, fwhm = 60 Hz), 143 (s, $CO_2$, fwhm = 360 Hz). MS (FAB): $m/z$ = 738 (M$^+$).

**Preparation of [($C_5H_4Me$)(CO)(NO)Mn($\mu_2$-$\eta^3$-CO$_2$)WCp$_2$][BF$_4$] (17).** Complex **17** was prepared as described above for complex **16** with $Cp_2W{=}O$ (118 mg, 0.360 mmol) and [($C_5H_4Me$)Mn(CO)$_2$(NO)][BF$_4$] (100 mg, 0.326 mmol) in acetone (30 mL) and was isolated as a brown solid in 83% yield (172 mg, 0.270 mmol). Anal. Calcd for $C_{18}H_{17}BF_4MnNO_4W$: C, 33.95; H, 2.67. Found: C, 33.74; H, 2.88. IR ($CH_2Cl_2$): $\nu_{CO}$ = 2024 (vs) cm$^{-1}$, $\nu_{NO}$ = 1784 (vs) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$): $\delta$ 5.99 (s, $C_5H_5$, 10 H), 5.55, 5.32, 5.12, 4.98 (s, $C_5H_4Me$, 4 H), 1.94 (s, $C_5H_4Me$, 3 H). $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 271.9 (s, $CO_2$), 225.7 (s, CO), 112.2 (s, $C_5H_4Me$), 98.1 (s, $C_5H_5$), 94.7, 94.0, 93.2, 92.7 (s, $C_5H_4Me$), 13.1 (s, $C_5H_4Me$).

**Preparation of [Cp*(CO)(NO)Re($\mu_2$-$\eta^3$-CO$_2$)MoCp$_2$][BF$_4$] (18).** Complex **18** was prepared as described above for complex **16** with $Cp_2Mo{=}O$ (54 mg, 0.222 mmol) and [Cp*Re(CO)$_2$(NO)][BF$_4$] (100 mg, 0.202 mmol) and was isolated as a brown solid in 77% yield (114 mg, 155 mmol). Anal. Calcd for $C_{22}H_{25}BF_4MoNO_4Re$: C, 35.89; H, 3.40. Found: C, 35.48; H, 3.59. IR ($CH_2Cl_2$): $\nu_{CO}$ = 1988 (vs) cm$^{-1}$, $\nu_{NO}$ = 1723 (vs) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$): $\delta$ 5.94 (s, $C_5H_5$, 10 H), 2.07 (s, $C_5Me_5$, 15 H). $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 243.1 (s, $CO_2$), 203.8 (s, CO), 106.0 (s, $C_5Me_5$), 103.1 (s, $C_5H_5$), 10.3 (s, $C_5Me_5$). MS (FAB): $m/z$ = 649 (M$^+$).

**Preparation of [($C_5H_4Me$)(CO)(NO)Mn($\mu_2$-$\eta^3$-CO$_2$)MoCp$_2$][BF$_4$] (19).** Complex **19** was prepared as described above for complex **16** with $Cp_2Mo{=}O$ (87 mg, 0.360 mmol) and [($C_5H_4Me$)Mn(CO)$_2$(NO)][BF$_4$] (100 mg, 0.326 mmol) in acetone as solvent and was isolated as a brown solid in 62% yield (119 mg, 0.202 mmol). Anal. Calcd for $C_{18}H_{17}BF_4MnMoNO_2$: C, 39.37; H, 3.10. Found: C, 39.19; H, 3.35. IR ($CH_2Cl_2$): $\nu_{CO}$ = 2017 (vs) cm$^{-1}$, $\nu_{NO}$ = 1770 (vs) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$): $\delta$ 5.96 (s, $C_5H_5$, 10 H), 5.32, 5.12, 5.08, 4.98 (s, $C_5H_4Me$, 4 H), 1.94 (s, $C_5H_4Me$, 3 H). $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 267.1 (s, $CO_2$), 226.8 (s, CO), 111.9

($C_5H_4$Me), 103.3 ($C_5H_5$), 94.6, 94.0, 93.2, 92.4 (s, $C_5H_4$Me), 13.1 (s, $C_5H_4$*Me*).

**Preparation of $[Cp(CO)_2Fe(\mu_2\text{-}\eta^3\text{-}CO_2)WCp_2][PF_6]$ (20).** Complex **20** was prepared as described above for complex **16** with $Cp_2W{=}O$ (109 mg, 0.33 mmol) and $[CpFe(CO)_3][PF_6]$ (105 mg, 0.30 mmol) in acetone as solvent and was isolated as a black solid in 95% yield (194 mg, 0.285 mmol). Anal. Calcd for $C_{18}H_{15}BF_6FeO_4PW$: C, 31.80; H, 2.20. Found: C, 31.85; H, 2.52. IR (acetone): $\nu_{CO}$ = 2047 (vs) $cm^{-1}$, 1996 (vs) $cm^{-1}$. $^1H$ NMR (acetone-$d_6$): $\delta$ 6.13 (s, $C_5H_5$, 10 H), 5.21 (s, $C_5H_5$, 5 H). $^{13}C$ NMR (acetone-$d_6$): $\delta$ 259.5 (s, $CO_2$), 211.9 (s, CO), 98.4 (s, $C_5H_5$), 87.7 (s, $C_5H_5$). $^{17}O$ NMR (20% $CD_3CN$/80% $CH_3CN$): $\delta$ 369 (s, CO, fwhm = 60 Hz), 168 (s, $CO_2$, fwhm = 170 Hz). MS (FAB): *m/z* = 534 ($M^+$).

**Preparation of $[Cp^*(CO)_2Ru(\mu_2\text{-}\eta^3\text{-}CO_2)WCp_2][BF_4]$ (21).** Complex **21** was prepared as described above for complex **16** with $Cp_2W{=}O$ (109 mg, 0.33 mmol) and $[Cp^*Ru(CO)_3][BF_4]$ (121 mg, 0.30 mmol) and was isolated as a brown solid in 97% yield (214 mg, 0.291 mmol). Anal. Calcd for $C_{23}H_{25}BF_4O_4RuW$: C, 37.48; H, 3.39. Found: C, 37.25; H, 3.81. IR ($CH_2Cl_2$): $\nu_{CO}$ = 2048 (vs) $cm^{-1}$, 1980 (vs) $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 5.92 (s, $C_5H_5$, 10 H), 1.89 (s, $C_5Me_5$, 15 H). $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 251.5 (s, $CO_2$), 199.0 (s, CO), 102.3 ($C_5Me_5$), 97.8 (s, $C_5H_5$), 10.1 (s, $C_5Me_5$).

**Preparation of $[\textit{trans}\text{-}(PEt_3)_2(Cl)Pt(\mu_2\text{-}\eta^3\text{-}CO_2)WCp_2][BF_4]$ (22).** Complex **22** was prepared as described above for complex **16** with $Cp_2W{=}O$ (216 mg, 0.665 mmol) and $[\textit{trans}\text{-}PtCl(PEt_3)_2(CO)][BF_4]$ (335 mg, 0.576 mmol) and was isolated as a brown solid in 38% yield (199 mg, 0.218 mmol). Anal. Calcd for $C_{23}H_{40}BClF_4O_2P_2PtW$: C, 30.26; H, 4.49. Found: C, 30.26; H, 4.44. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 5.94 (s, $C_5H_5$, 10 H), 1.88 (m, $CH_2CH_3$, 12 H), 1.09 (m, $CH_2CH_3$, 18 H). $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 211.8 (t, $CO_2$, $J_{PC}$ = 6 Hz, $J_{PtC}$ = 713 Hz), 97.60 (s, $C_5H_5$), 15.22 (t, $CH_2CH_3$, $J_{PC}$ = 17 Hz), 8.39 (s, $CH_2CH_3$). $^{31}P$ NMR ($CD_2Cl_2$): $\delta$ 21.49 ($J_{PtP}$ = 1306 Hz).

**Crystallographic Characterization of $[Cp^*(CO)(NO)Re(\mu_2\text{-}\eta^3\text{-}CO_2)WCp_2][BF_4]$ (16).** Crystallographic data are summarized in Table I. A deep orange-brown crystal (0.10 × 0.18 × 0.35 mm) was mounted on a glass fiber. Photographic evidence and systematic absences in the reflection data indicated either of the space groups *Cc* and *C*2/*c*. The latter, centrosymmetric, alternative was chosen initially and subsequently verified by the results of refinement. An empirical correction for absorption ($\psi$ scan, 216 data) was applied. In order to minimize overlap of adjacent reflections due to the ~50-Å axis, a narrow scan width of 0.8 Å was used.

The structure was solved by direct methods, which found the positions of all eight metal atoms in four independent but chemically similar cations (molecules A–D). To conserve data, the Cp and Cp* rings were constrained to rigid pentagons, and the carbon atoms were isotropically refined. Additionally, two of the four independent $BF_4$- ions required tetrahedral constraint to deal with disorder problems. Hydrogen atoms were ignored. All computer software and sources of neutral-atom scattering factors are contained in the SHELXTL (5.1) software library (G. Sheldrick, Nicolet XRD Corp., Madison, WI).

**Crystallographic Characterization of $Cp_2Mo\{\eta^2(O,N)\text{-}OC(O)NPh\}$ (3).** Crystallographic data are summarized in Table I. An orange crystal (0.26 × 0.27 × 0.33 mm) was mounted on a glass fiber. Systematic absences in the diffraction data uniquely determined the monoclinic space group $P2_1/c$. No correction for absorption was required. The structure was solved by heavy-atom methods and refined with anisotropic thermal parameters. All hydrogen atoms were found and isotropically refined. The software used is as in **16** above.

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**Supplementary Material Available:** For **3** and **16** tables of anisotropic temperature factors and complete bond lengths and bond angles and for **3** a table of calculated hydrogen atom positions (14 pages); lists of structure factors for **3** and **16** (56 pages). Ordering information is given on any current masthead page.