spectral data acquired for 45 min at each temperature. The final temperature was 28 °C.

Attempts To Isolate the Intermediate in the Reaction of 1 with CS_2. The above reaction was repeated except at −10 °C the solvents were removed under vacuum resulting in isolation of the compound $Pt_2(S)(CO)_2(P\text{-}t\text{-}Bu_2Ph)_2$. This was crystallized from CH_2Cl_2/hexane solution: ^{31}P NMR (CH_2Cl_2 at 25 °C) δ 71.16, $|^1J(^{31}P, ^{195}Pt)| = 3173$ Hz, $|^2J(^{31}P,^{195}Pt)| = 129$ Hz, $|^3J(^{31}P,^{31}P)| = 129$ Hz; IR (Nujol mull) $\nu(C{=}O)$ 2010 (s), 1969 (w) cm^{-1}. Anal. Calcd for $Pt_2SP_2O_2C_{30}H_{46}$: C, 39.0; H, 5.0; S, 3.5; P, 6.7. Found: C, 38.9; H, 5.0; S, 3.6; P, 6.8.

Reaction of 1 with OCS. 1 (0.100 g, 0.078 mmol) was dissolved in 10 mL of toluene, and OCS was bubbled through the solution for 5 min, followed by stirring under an atmosphere of OCS for 12 h. The volume was reduced to 1–2 mL, and hexane was added. The yellow-brown precipitate was filtered, washed with diethyl ether, and dried in air; yield 82%. It was characterized by ^{31}P NMR and IR spectroscopy as $Pt_2(S)(CO)_2(P\text{-}t\text{-}Bu_2Ph)_2$ (**4**).

Preparation of $Pt_2(SO_2)(CO)_2(P\text{-}t\text{-}Bu_2Ph)_2$ (5). 1 (0.10 g, 0.075 mmol) was dissolved in 10 mL of toluene. SO_2 was bubbled through it for 1 min, and the volume was then reduced to 1–2 mL. The addition of hexane under a CO atmosphere gave yellow crystals which were filtered, washed with diethyl ether, and dried in air: yield 75%; ^{31}P NMR (CH_2Cl_2 at 25 °C) δ 58.73, $|^1J(^{31}P,^{195}Pt)| = 3980$ Hz, $|^2J(^{31}P,^{195}Pt)| = 328$ Hz, $|^3J(^{31}P,^{31}P)| = 76$ Hz; IR (Nujol mull) $\nu(C{=}O)$ 2040 (s), 2001 (w) (SO_2) cm^{-1}, 1049 (w), 1067 (m), 1180 (m) cm^{-1}. Anal. Calcd for $Pt_2S_1P_2O_4C_{30}H_{46}$: C, 37.7; H, 4.8; P, 6.5; S, 3.3. Found: C, 38.6; H, 5.1; P, 6.5; S, 3.5.

Preparation of $Pt_3(SO)(CO)_2(P\text{-}t\text{-}Bu_2Ph)_3$ (6). **5** (0.025 g) was dissolved in 5 mL of CH_2Cl_2/hexane solution and allowed to stand for a period of 2 weeks, during which time yellow-orange crystals were formed: yield 75%; ^{31}P NMR (CH_2Cl_2 at 25 °C) δ 83.6 (d, 49 Hz), $|^1J(^{195}Pt,^{31}P)| = 4395$ Hz, $|^2J(^{195}Pt,^{31}P)| = 394$ Hz, δ 103.8 (t, 49 Hz), $|^1J(^{195}Pt,^{31}P)| = 4395$ Hz, $|^2J(^{195}Pt,^{31}P)| = 479$ Hz; IR (Nujol mull) $\nu(C{=}O)$ 1811 (s), 1847 (s) (SO_2) cm^{-1}, 1060 (s), 1203 (m) cm^{-1}. Anal. Calcd for $Pt_3SP_3O_4C_{44}H_{69}$: C, 38.5; H, 5.0; P, 6.8; S, 2.3. Found: C, 38.3; H, 5.0; P, 6.9; S, 2.3.

Characterization of $Pt_3(CO)(SO_2)_2(P\text{-}t\text{-}Bu_2Ph)_3$ (7). Complex 1 was observed in ^{31}P NMR and IR spectra as a minor product (5%) from the reaction of 1 and SO_2 at 25 °C. We were unable to separate this complex from the mixture to obtain analytically pure samples: ^{31}P NMR (toluene at 25 °C) δ 87.7 (d, 51 Hz), $|^1J(^{195}Pt,^{31}P)| = 4476$ Hz, $|^2J(^{195}Pt,^{31}P)| = 420$ Hz, δ 64.8 (t, 56 Hz), $|^1J(^{195}Pt,^{31}P)| = 4476$ Hz, $|^2J(^{195}Pt,^{31}P)| = 327$ Hz; IR (Nujol mull) $\nu(C{=}O)$ 1857 (s), 1730 (s) cm^{-1}.

Acknowledgment. We thank the University of Toronto and the Natural Sciences and Engineering Council of Canada for operating and equipment grants and Johnson Matthey and Co. Ltd. for their loan of Pt salts. We also wish to thank N. Plavac for his assistance in recording the NMR data, W. Mason for technical assistance, and Prof. A. J. Poë for helpful discussions.

Registry No. **1**, 62931-81-1; **2**, 62987-80-8; **3**, 97689-47-9; **4**, 97689-48-0; **5**, 97703-27-0; **6**, 97719-79-4; **7**, 97703-28-1; $Pt_3(CO)_3(P\text{-}t\text{-}Bu_3)_2(PCy_3)$, 71080-86-9; $Pt_3(CO)_3(P\text{-}t\text{-}Bu_2Ph)_2(PCy_3)$, 97689-49-1; $Pt_3(CO)_3(P\text{-}i\text{-}Pr_3)_3$, 71080-84-7; $Pt_3(CO)_3(P\text{-}t\text{-}BuPh_2)_3$, 71080-85-8; PCy_3, 2622-14-2; $P\text{-}i\text{-}Pr_3$, 6476-36-4; $P\text{-}t\text{-}Bu_2Ph$, 32673-25-9; $P\text{-}t\text{-}BuPh_2$, 6002-34-2; $Pt_2(CS_2)_2(P\text{-}t\text{-}Bu_2Ph)_2$, 91686-59-8.

Oxidative Addition of Cyclopropenyl Cations to Zerovalent Molybdenum and Tungsten Centers. Synthesis of η^3-Cyclopropenyl and η^3-Oxocyclobutenyl Complexes of Molybdenum(II) and Tungsten(II). Crystal and Molecular Structures of $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3Ph_2R)(CO)_2]$ (R = Ph, *t*-Bu)

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Oxidative addition of triphenylcyclopropenyl *hexafluorophosphate* to $[Mo(CO)_3(MeCN)_3]$ affords the cationic cyclopropenyl complex $[Mo(\eta\text{-}C_3Ph_3)(CO)_2(MeCN)_3]^+[PF_6^-]$, **8**, which reacts with cyclopentadienylthallium to give excellent yields of the neutral η^3-cyclopropenyl complex $[Mo(\eta\text{-}C_3Ph_3)(\eta\text{-}C_5H_5)(CO)_2]$, **6a**. Similar one-pot syntheses of the analogous complexes $[M(\eta\text{-}C_3Ph_2\text{-}t\text{-}Bu)(\eta\text{-}C_5H_5)(CO)_2]$ (**6b**, M = Mo; **6c**, M = W) from the *tert*-butyldiphenylcyclopropenyl cation are described. In contrast, use of triphenylcyclopropenyl *chloride* or *bromide* in the reaction with $[M(CO)_3(MeCN)_3]$ (M = Mo, W) affords ultimately the ring-expanded oxocyclobutenyl compounds **9**, presumably via intermediates **10**. Thermal reaction of the (triphenylcyclopropenyl)molybdenum complex **6a** with PMe_2Ph or $P(OPh)_3$ results in ring expansion to give the oxocyclobutenyl complexes **11**. The dynamic behavior of the cyclopropenyl ligands in compounds **6** is reported, and compounds **6a** and **6b** have been characterized by single-crystal X-ray diffraction studies: **6a** crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.545$ (2) Å, $b = 16.580$ (3) Å, $c = 14.463$ (3) Å, $\beta = 98.47$ (2)°, and $Z = 4$; **6b** crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.488$ (2) Å, $b = 16.394$ (4) Å; $c = 16.168$ (4) Å, $\beta = 95.28$ (2)°, and $Z = 4$. Both compounds clearly contain η^3-cyclopropenyl ligands, and their structures are compared and contrasted with those of other cyclopropenyl and metallacyclobutadiene complexes.

Introduction

A mechanism for transition-metal-catalyzed alkyne metathesis involving transition metal–alkylidyne and metallacyclobutadiene intermediates was proposed by Katz in 1975.[3] More recently, Schrock has synthesized a number of tungsten–alkylidyne complexes and has found that they catalyze the metathesis of alkynes,[4] with activities far

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(2) Alfred P. Sloan Research Fellow 1980–1984.

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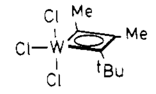
greater than those reported for heterogeneous[5] or homogeneous Mo(CO)$_6$/phenol[6] catalysts. Schrock has also shown that the stoichiometric reaction of the alkylidyne complex 1 with 1 equiv of 2-butyne produced the planar, delocalized metallacyclobutadiene complex 2, which was characterized crystallographically.[7] Subsequently, a number of analogues of 2 containing different ring substituents and/or containing alkoxy ligands were synthesized, structurally characterized as planar metallacyclobutadienes, and shown to metathesize alkynes.[8] An interesting side reaction, resulting in catalyst deactivation, was shown to involve formation of η^5-cyclopentadienyl complexes.[8c] The relative location of substituents in the metallacyclobutadiene precursors and the product cyclopentadienyl ligands led to the suggestion that η^3-cyclopropenyl ligands might be intermediates in this reaction.[8c] The cyclopropenyl–metal bond represents a valence isomer of the metallacyclobutadiene framework and in terms of a purely organic analogy can be thought of as a metallatetrahedrane. Definition of the factors influencing the interconvertibility of metallacyclobutadiene and metallatetrahedrane valence isomers therefore represents an interesting challenge for synthetic and theoretical chemists.

In contrast to the chemistry of 1, and its alkoxy analogues, the same workers showed that the cyclopentadienyl analogue 3 reacted with diphenylacetylene to afford the metallacyclobutadiene compound **4a**.[9] Notably the metallacyclobutadiene ring in **4a** contained localized double and single bonds and was severely puckered, having a ground-state geometry intermediate between the planar ring encountered in 2 and an elongated "metallatetrahedrane" or η^3-cyclopropenyl–tungsten bond. Also notable was the fact that the added alkyne had been cleaved to give the observed structure in which the phenyl groups were no longer on adjacent carbon atoms. In solution **4a** was fluxional, exhibiting a single broad resonance for all three ring carbon atoms in the $^{13}C\{^1H\}$ NMR spectrum at room temperature; cleavage of the original alkyne and the solution scrambling of carbon environments was suggested to occur via a W(VI) "metallatetrahedrane" intermediate,[9] another canonical form of which is best described by an (η^3-cyclopropenyl)tungsten(IV) interaction.

In agreement with the hypothesis that a metallacyclobutadiene complex might undergo facile conversion to an η^3-cyclopropenyl compound, **4b** was shown to react with PMe$_3$ to form the crystallographically characterized complex 5.[10] Interestingly, NMR studies of 5 showed that the C$_3$ ring did not rotate rapidly about the metal–ring axis on the NMR time scale at room temperature. Similarly, addition of nitrogen donor ligands to planar metallacyclobutadiene complexes 2 resulted in ring closure to yield the η^3-cyclopropenyl compounds WCl$_3$(η-C$_3$Me$_2$-*t*-Bu)L$_2$ (L = pyridine [two isomers], L$_2$ = tetramethylethylenediamine); the TMEDA compound was characterized by X-ray crystallography.[8c,11]

${}^{t}\mathrm{BuC{\equiv}WCl_3(dme)}$

1



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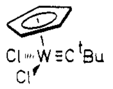

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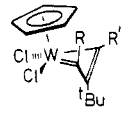
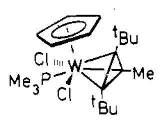


4 a. R = R' = Ph
b. R = Me; R = ^{t}Bu



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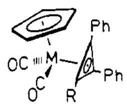

6 a. M = Mo; R = Ph
b. M = Mo; R = ^{t}Bu
c. M = W ; R = ^{t}Bu

In contrast to its ubiquitous acyclic analogue the η-allyl ligand, relatively few transition-metal complexes containing unambiguously characterized η^3-cyclopropenyl ligands have been reported.[8c,11–23] We have been interested in the reactions of cyclopropenyl cations with transition-metal centers for some time, and in view of recent results (vide supra) it seemed appropriate to establish whether the ground-state structures of other C$_3$R$_3$–metal compounds should best be represented as η^3-cyclopropenyl or metallacyclobutadiene (planar or puckered) forms and how facile any interconversion between these isomers might be. Theoretical studies of this interconversion have appeared,[24,25] and crystallographically characterized examples of metallacyclobutadiene complexes of rhodium[26] and iridium[27] have also been reported.

As an initial probe we chose to investigate the effect of oxidation state on the ground-state structures of C$_3$R$_3$ complexes of group 6[41] metals and here report the results

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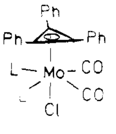
of an investigation of the synthesis and molecular structure of **6a**[19] and some of its relatives, which appeared to be the closest analogues of the puckered metallacyclobutadiene complex **4a**. A preliminary account of some aspects of this work has appeared.[21]

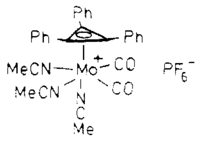
Results

In 1968 Hayter reported briefly on the low yield synthesis (3% overall) of a complex thought to have structure **6a**, from the oxidative addition reaction of $Mo(CO)_3(MeCN)_3$ with the *chloride* salt of the triphenylcyclopropenyl cation, followed by treatment of the putative intermediate **7a** with cyclopentadienyllithium.[19] Only ^1H NMR data were reported for **6a**, but an analogue (**7b**) of the reaction intermediate **7a** was later prepared in a similar fashion and characterized crystallographically by other workers.[20]

In our hands, the reaction of $Mo(CO)_3(MeCN)_3$ with triphenylcyclopropenyl *hexafluorophosphate* in refluxing acetonitrile followed by evaporation of the solvent and treatment of the crude residue with cyclopentadienylthallium in THF solution afforded a one-pot synthesis (60% overall yield) of an air-sensitive orange material whose spectroscopic properties were consistent with those reported by Hayter[19] and which was subsequently characterized crystallographically as having structure **6a** in the solid state (see below). The most notable spectroscopic property of **6a** was found to be a single ^{13}C NMR resonance for all three ring carbon atoms of the C_3Ph_3 ligand, even at −80 °C. The complex also exhibited two strong metal carbonyl IR bands at 1971 and 1912 cm^{-1}. Interruption of the reaction after the first step and recrystallization of the residue yielded the cationic complex 8 as its PF_6^- salt.



7 a. L=MeCN
b. L_2 = bipy



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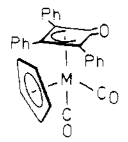
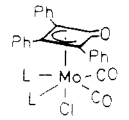
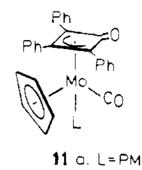


9 a. M=Mo
b. M=W



10 a. L=MeCN
b. L_2= bipy



11 a. L=PMe_2Ph
b. L=$P(OPh)_3$

Complex 8 exhibited two equal intensity carbonyl stretching bands and two nitrile bands of unequal intensity in its IR spectrum, characteristic of local C_{3v} symmetry for the $Mo(MeCN)_3$ group. In addition, 8 possessed two methyl resonances of ratio 2:1 in its ^1H NMR spectrum, and a $^{13}C\{^1H\}$ NMR spectrum which contained a single resonance for the three cyclopropenyl carbon atoms, a single resonance for the carbonyl carbons, and two methyl resonances. Appropriate phenyl group NMR resonances were also observed. The only isomeric possibility for 8 appears to be that illustrated, with a rigid coordination geometry about the Mo center and free rotation of the C_3Ph_3 ligand about the Mo–C_3 axis. Subsequent treatment of pure 8 with cyclopentadienylthallium afforded **6a** in 93% yield.

Substitution of *tert*-butyldiphenylcyclopropenyl hexafluorophosphate in the reaction sequence similarly afforded good yields of **6b**; this compound was spectroscopically compatible with **6a**, and its solid-state structure was also determined crystallographically (see below). Compound **6b** exhibited two ^{13}C NMR resonances for the C_3 ring carbon atoms at −80 °C. The tungsten analogue of **6a** could not be generated by using the hexafluorophosphate salt of the triphenylcyclopropenyl cation; under these conditions only unreacted $W(CO)_3(MeCN)_3$ was recovered. However, the *tert*-butyldiphenylcyclopropenyl cation did react to produce ultimately the cyclopropenyltungsten compound **6c**, whose spectroscopic properties clearly showed it to be isostructural with its molybdenum analogue **6b** and which also exhibited only two ^{13}C NMR resonances for the C_3 ring carbon atoms at −80 °C.

In some cases modification of the reaction scheme outlined above by adding halide ion in the oxidative addition step afforded different results. Reaction of $Mo(CO)_3(MeCN)_3$ with the triphenylcyclopropenyl cation in the presence of chloride or bromide ion, followed by addition of cyclopentadienylthallium yielded only traces of **6a**, the major product being an air-stable yellow crystalline complex, identified by its spectroscopic properties as having structure **9a**. The IR spectrum of this material exhibited metal carbonyl stretches at 2001 and 1945 cm^{-1}, significantly higher frequencies than those in **6a**, and a medium intensity band at 1677 cm^{-1} characteristic of the oxocyclobutenyl ring ketone.[20,28] Appropriate NMR spectral data were also obtained. The intermediate in this reaction sequence is assumed to be **10a**, an analogue of which **10b** has been crystallographically characterized.[20] In contrast to the lack of reactivity observed between $W(CO)_3(MeCN)_3$ and triphenylcyclopropenyl hexafluorophosphate (vide supra), addition of bromide ion to the reaction mixture resulted in modest yields of the (oxocyclobutenyl)tungsten complex **9b**. Addition of halide ion to the reactions between $M(CO)_3(MeCN)_3$ (M = Mo, W) and the *tert*-butyldiphenylcyclopropenyl cation had no effect, and only **6b** or **6c** were obtained as the final products.

The triphenylcyclopropenylmolybdenum complex **6a** also underwent a thermal reaction with dimethylphenylphosphine or triphenyl phosphite to yield the ring-expanded oxocyclobutenyl compounds **11a** and **11b**, respectively. These compounds exhibited only a single metal carbonyl stretching band in the IR spectrum, along with the characteristic ketone vibration of the oxocyclobutenyl ring. The ^1H NMR spectrum of **11a** showed two doublet resonances for the methyl groups of the phosphine ligand, demonstrating the absence of a molecular symmetry plane. In contrast, the *tert*-butyldiphenylcyclopropenyl analogue **6b** did not react with dimethylphenylphosphine under thermal (benzene, 80 °C) or photochemical (450-W Hanovia lamp; Pyrex flask) conditions to give either ring expansion or ligand substitution chemistry.

In order to place the structures of these C_3R_3 complexes on a firm footing, **6a** and **6b** were subjected to single-crystal X-ray crystallographic analyses. Details of the crystallographic determinations are assembled in Table I. ORTEP drawings and atom numbering schemes of **6a** and **6b** are presented in Figures 1 and 2, and atomic coordinates are shown in Tables II (**6a**) and III (**6b**). Selected bond dis-

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Table I. Crystal, Data Collection, and Refinement Data for $CpMo(CO)_2[\eta^3\text{-}C_3(C_6H_5)_3]$ (6a) and $CpMo(CO)_2[\eta^3\text{-}C_3(C_6H_5)_2(t\text{-}C_4H_9)]$ (6b)

	$CpMo(CO)_2[\eta^3\text{-}C_3(C_6H_5)_3]$ (**6a**)	$CpMo(CO)_2[\eta^3\text{-}C_3(C_6H_5)_2\text{-}(t\text{-}C_4H_9)]$ (**6b**)
formula	$C_{28}H_{20}MoO_2$	$C_{26}H_{23}MoO_2$
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	9.545 (2)	8.488 (2)
b, Å	16.580 (3)	16.394 (4)
c, Å	14.463 (3)	16.168 (4)
β, deg	98.47 (2)	95.28 (2)
V, Å^3	2264.0 (9)	2240.1 (9)
Z	4	4
ρ(calcd), g cm^{-3}	1.421	1.374
μ, cm^{-1}	5.85	5.87
diffractometer	Nicolet R3	
radiation	Mo Kα = (λ = 0.710 73)	
collection technique	ω	ω
scan range, deg	$4 \leqslant 2\theta \leqslant 45$	$4 \leqslant 2\theta \leqslant 48$
unique data	3292 (3450 collected)	3524 (3808 collected)
unique data $F \geqslant n\sigma(F_o)$	2747 (n = 3)	2773 (n = 3)
cryst dimens, mm	0.30 × 0.31 × 0.31	0.27 × 0.28 × 0.30
standard rflns	3/97 (2% decay)	3/97 (7% decay)
R_F, R_{wF}, GOF	0.0311, 0.0386, 1.412	0.0395, 0.0430, 1.119
highest peak, final diff map, e Å^{-3}	0.31	0.30
no. of parameters refined	260	263

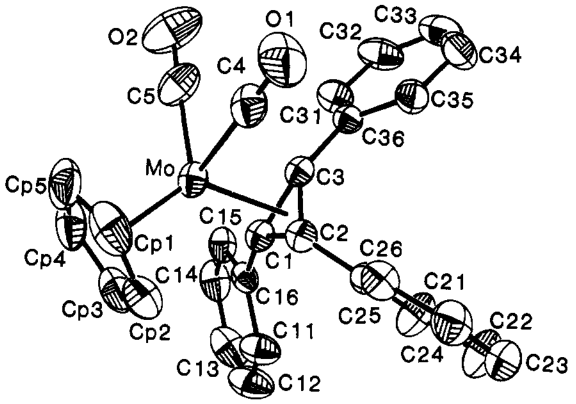

Figure 1. ORTEP drawing and atom numbering scheme for **6a**.

tances and angles for both complexes are presented in a comparative fashion in Table IV. Additional crystallographic data and full tables of bond distances and angles are available as supplementary material.[29]

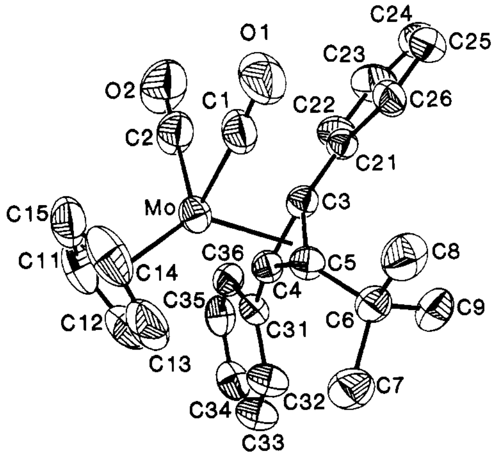

Figure 2. ORTEP drawing and atom numbering scheme for **6b**.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for 6a

atom	x	y	z	U
Mo	4231 (1)	7165 (1)	4052 (1)	39 (1)[a]
O(1)	3423 (4)	8622 (2)	5237 (2)	91 (1)[a]
O(2)	1369 (4)	6497 (3)	4555 (3)	112 (2)[a]
Cp(1)	6407 (5)	7105 (3)	4993 (3)	73 (2)[a]
Hp(1)	6674	7533	5430	68
Cp(2)	6706 (4)	7093 (3)	4069 (3)	70 (2)[a]
Hp(2)	7218	7497	3778	60
Cp(3)	6096 (5)	6389 (3)	3649 (3)	70 (2)[a]
Hp(3)	6150	6223	3020	60
Cp(4)	5458 (5)	5964 (3)	4309 (3)	75 (2)[a]
Hp(4)	4964	5459	4217	60
Cp(5)	5658 (5)	6409 (3)	5150 (3)	75 (2)[a]
Hp(5)	5344	6273	5732	60
C(1)	3601 (4)	7217 (2)	2516 (2)	38 (1)[a]
C(2)	4074 (3)	8001 (2)	2891 (2)	38 (1)[a]
C(3)	2642 (4)	7718 (2)	2905 (2)	36 (1)[a]
C(4)	3696 (4)	8092 (2)	4791 (3)	55 (1)[a]
C(5)	2416 (5)	6719 (3)	4346 (3)	68 (2)[a]
C(11)	4613 (2)	6806 (1)	1114 (2)	59 (1)[a]
C(12)	4587 (2)	6325 (1)	320 (2)	80 (2)[a]
C(13)	3584 (2)	5712 (1)	138 (2)	75 (2)[a]
C(14)	2606 (2)	5580 (1)	750 (2)	63 (2)[a]
C(15)	2632 (2)	6061 (1)	1544 (2)	48 (1)[a]
C(16)	3636 (2)	6674 (1)	1726 (2)	39 (1)[a]
C(21)	4319 (3)	8981 (1)	1643 (1)	63 (2)[a]
C(22)	4779 (3)	9722 (1)	1343 (1)	75 (2)[a]
C(23)	5543 (3)	10246 (1)	1982 (1)	67 (2)[a]
C(24)	5846 (3)	10030 (1)	2922 (1)	62 (2)[a]
C(25)	5389 (3)	9290 (1)	3223 (1)	48 (1)[a]
C(26)	4624 (3)	8765 (1)	2584 (1)	38 (1)[a]
C(31)	80 (7)	7516 (3)	2357 (5)	54 (4)[a]
C(32)	−1284 (7)	7829 (3)	2133 (5)	76 (5)[a]
C(33)	−1531 (7)	8646 (3)	2272 (5)	82 (6)[a]
C(34)	−414 (7)	9150 (3)	2636 (5)	76 (5)[a]
C(35)	950 (7)	8837 (3)	2861 (5)	52 (4)[a]
C(36)	1197 (7)	8020 (3)	2721 (5)	39 (3)[a]

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

Discussion

The molecular structures of **6a** and **6b** clearly show them to be η^3-cyclopropenyl complexes rather than metallacyclobutadienes. Each of the C_3 ring carbon atoms is bound to the molybdenum, forming an elongated tetrahedron with slightly unsymmetrical coordination in each case being reflected in small differences in the Mo–carbon and carbon–carbon distances. Distances from Mo to the centroids of the cyclopentadienyl rings are identical for both compounds, as are the distances from Mo to the C_3 ring centroids. Notably, the Mo–C_5 centroid distances are ca. 0.06 Å shorter than the Mo–C_3 centroid separations. Comparisons of metal–C_5 and metal–C_3 centroid distances in other crystallographically characterized η^3-cyclopropenyl compounds are provided in Table V. It has been noted that the tungsten–C_3 carbon distances in the formally W(IV)–cyclopropenyl complex **5** are ca. 0.05 Å shorter than those to the C_5 ring carbons,[10] whereas the opposite is true for the Ni(II) compound $Ni(C_3Ph_3)(C_5H_5)$.[15] The relative metal–ring distances in compounds **6a** and **6b** are clearly more closely related to the nickel complex than to **5**. The ring substituents are displaced from the plane of the C_3 ring, away from the metal. The "bend-back angles" defined as the angle between the substituent to ring carbon bond and vector from the ring carbon to the C_3 ring centroid also are listed in Table V along with analogous values for some other η^3-cyclopropenyl complexes. It has been suggested

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[29] See note at end of text regarding supplementary material.

Table III. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for 6b

atom	x	y	z	U^a
Mo	485 (1)	2137 (1)	3880 (1)	49 (1)
O(1)	−1565 (4)	3514 (2)	4577 (2)	97 (2)
O(2)	−2751 (4)	1425 (3)	3137 (3)	120 (2)
C(1)	−817 (5)	3025 (3)	4292 (3)	65 (2)
C(2)	−1546 (5)	1685 (3)	3402 (3)	73 (2)
C(3)	94 (4)	2828 (2)	2657 (2)	46 (1)
C(4)	1373 (4)	2283 (2)	2644 (2)	47 (1)
C(5)	1566 (4)	3044 (2)	3114 (2)	48 (1)
C(6)	2593 (5)	3798 (2)	3154 (3)	55 (1)
C(7)	4274 (5)	3608 (3)	3527 (3)	78 (2)
C(8)	1900 (6)	4450 (3)	3684 (3)	77 (2)
C(9)	2653 (5)	4121 (3)	2265 (3)	73 (2)
C(11)	1369 (6)	870 (3)	4339 (3)	84 (2)
C(12)	2694 (6)	1308 (3)	4173 (3)	86 (2)
C(13)	2832 (7)	1956 (3)	4746 (4)	96 (2)
C(14)	1565 (7)	1901 (4)	5228 (3)	93 (2)
C(15)	666 (6)	1243 (3)	4982 (3)	86 (2)
C(21)	−1244 (4)	3166 (2)	2146 (2)	46 (1)
C(22)	−1874 (5)	2772 (3)	1432 (3)	63 (2)
C(23)	−3095 (6)	3118 (4)	925 (3)	84 (2)
C(24)	−3724 (5)	3848 (4)	1118 (3)	78 (2)
C(25)	−3145 (5)	4237 (3)	1827 (3)	70 (2)
C(26)	−1915 (5)	3909 (2)	2339 (3)	58 (1)
C(31)	2121 (4)	1728 (2)	2088 (2)	48 (1)
C(32)	1219 (5)	1150 (2)	1632 (2)	56 (1)
C(33)	1904 (6)	640 (3)	1081 (3)	66 (2)
C(34)	3491 (6)	690 (3)	1000 (3)	70 (2)
C(35)	4394 (6)	1253 (3)	1453 (3)	78 (2)
C(36)	3718 (5)	1767 (3)	2001 (3)	66 (2)

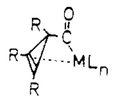
[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Selected Bond Distances and Angles for 6a and 6b[a]

$CpMo(CO)_2[\eta^3\text{-}C_3(C_6H_5)_3]$ (**6a**)		$CpMo(CO)_2[\eta^3\text{-}C_3(C_6H_5)_2(t\text{-}C_4H_9)]$ (**6b**)	
	(a) Bond Distances (Å)		
Mo–CNT(1)	1.997 (4)	Mo–CNT(1)	1.999 (4)
Mo–CNT(2)	2.055 (4)	Mo–CNT(2)	2.067 (4)
Mo–C(4)	1.982 (4)	Mo–C(2)	1.968 (4)
Mo–C(5)	1.986 (5)	Mo–C(1)	1.980 (4)
Mo–C(1)	2.215 (3)	Mo–C(4)	2.213 (4)
Mo–C(3)	2.270 (3)	Mo–C(3)	2.276 (4)
Mo–C(2)	2.165 (3)	Mo–C(5)	2.191 (4)
C(4)–O(1)	1.147 (6)	C(1)–O(1)	1.145 (6)
C(5)–O(2)	1.143 (5)	C(2)–O(2)	1.153 (6)
C(1)–C(2)	1.454 (4)	C(4)–C(5)	1.462 (5)
C(2)–C(3)	1.448 (5)	C(5)–C(3)	1.437 (5)
C(1)–C(3)	1.413 (5)	C(3)–C(4)	1.407 (5)
	(b) Bond Angles (deg)		
CNT(1)–Mo–CNT(2)	128.6 (2)	CNT(1)–Mo–CNT(2)	131.1 (2)
CNT(1)–Mo–C(4)	121.4 (2)	CNT(1)–Mo–C(1)	119.4 (2)
CNT(1)–Mo–C(5)	120.3 (2)	CNT(1)–Mo–C(2)	118.2 (2)
CNT(2)–Mo–C(4)	96.9 (2)	CNT(2)–Mo–C(1)	96.6 (2)
CNT(2)–Mo–C(5)	95.4 (2)	CNT(2)–Mo–C(2)	95.3 (2)
C(4)–Mo–C(5)	82.6 (2)	C(1)–Mo–C(2)	85.0 (2)
C(1)–C(2)–C(3)	58.3 (3)	C(4)–C(5)–C(3)	58.0 (3)
C(2)–C(3)–C(1)	61.1 (3)	C(5)–C(3)–C(4)	61.9 (3)
C(3)–C(1)–C(2)	60.6 (3)	C(3)–C(4)–C(5)	60.1 (3)
C_5 plane-to-C_3 plane	53.6 (4)	C_5 plane-to-C_3 plane	52.1 (4)

[a] Comparable parameters on same line. CNT(1) = centroid of C_5 ring. CNT(2) = centroid of C_3 ring.

that larger substituent bend-back angles, together with shorter metal–carbon distances, may be characteristic of a "metallatetrahedrane" structure.[10] In compounds **6a** and **6b** it is interesting that the C_3 ring carbon atom most closely bound to the metal [C(2) in **6a** and C(5) in **6b**] is the one opposite the shortest carbon–carbon bond within the ring, perhaps indicating some localized σ–π ring–metal bonding; furthermore the substituent bend-back angle associated with the shortest Mo–C bond is significantly larger (ca. 10°) than those for the other two substituents. While we do not have a satisfactory explanation for this phenomenon, it does serve to emphasize that while there appears to be a correlation between larger bend-back angles and shorter M–C distances *within individual compounds*, there are dramatic variations in bend-back angles between different compounds. Finally, the bend-back angles in **6a** and **6b** can be compared with those observed in the crystallographically characterized (η^2-cyclopropene)molybdenum complex **13**.[34] The phenyl groups attached to the coordinated olefin of **13** bend back by 39.7° and 36.9°; the corresponding angle at the saturated cyclopropene carbon atom is 57.4°.



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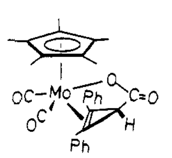
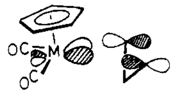
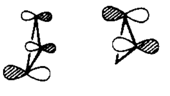


13

In solution the C_3 ring in compounds **6a**, **6b**, and **6c** rotates rapidly about the metal–ring axis on the NMR time scale at −80 °C, as indicated by the observation of only a single ^{13}C resonance for the three ring carbons of **6a** and two resonances for the three ring carbons of **6b** and **6c**. If the solid-state conformation were maintained in solution, two such resonances would be expected for **6a** and three each for **6b** and **6c**. A theoretical prediction of 6.7 kcal mol^{-1} for the ring rotation barrier in the hypothetical molecule $[Fe(\eta^3\text{-}C_3H_3)(CO)_3]^-$ has been made.[30] The C_3 rings in the isoelectronic molecules $[Fe(\eta^3\text{-}C_3Ph_2R)(CO)_2(NO)]$ (R = Ph, t-Bu) and $[Co(\eta^3\text{-}C_3Ph_3)(CO)_2(PPh_3)]$ also rotate rapidly on the NMR time scale at low temperatures,[23] so this number may be a realistic one. Compounds **6** differ from their W(IV) relatives[10,11] in which the corresponding C_3 ring rotation can be "frozen out" on the NMR time scale. The reason for this difference is unclear but may relate in part to the shorter W–C_3 separation in the W(IV) compounds (see Table V) giving rise to an increased steric hindrance to rotation. The facility of C_3 rotation in **6a**, **6b**, and **6c** also contrasts markedly with relatively high rotation barrier in isoelectronic, acyclic allyl analogues, in which exo and endo isomers can be isolated. An extended Hückel MO description of the bonding in these latter compounds has appeared.[40] One of the principal orbital interactions in the acyclic allyl compounds is that between the n orbital of the allyl fragment and the a″ orbital of the $CpMo(CO)_2$ fragment, as shown in **14**.



14



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(30) Albright, T. A.; Hoffmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* 1977, *99*, 7546.

Table V. Comparison of M-C_3 Centroid Distances and C_3 Substituent Bend-Back Angles for Some η^3-Cyclopropenyl Complexes

complex	M-C_3 centroid,[a] Å	bend-back angles,[b] deg	ref
$Ni(C_3Ph_3)(C_5H_5)$	1.96	20.1, 19.2, 19.7	15
$Co(C_3Ph_3)(CO)_3$	2.01	20.3, 22.2, 15.9	18
$Mo(C_3Ph_3)(CO)_2(bpy)Br$ (**7b**)	2.06	21.6, 32.5, 24.1	20
$W(C_5H_5)(C_3$-*t*-$Bu_2Me)(PMe_3)Cl_2$ (**5**)	1.99	25.2 (Me), 36.7 (*t*-Bu), 29.5 (*t*-Bu)	10
$W(C_3Me_2$-*t*-$Bu)(TMEDA)Cl_3$	1.92	43.5 (Me), 25.6 (Me), 35.3 (*t*-Bu)	8c, 11
$Mo(C_3Ph_3(C_5H_5)(CO_2)$ (**6a**)	2.05	24.7 (Ph-C(1)), 26.6 (Ph-C(3)), 34.4 (Ph-C(2))	this work
$Mo(C_3$-*t*-$BuPh_2)(C_5H_5)(CO)_2$ (**6b**)	2.07	21.7 (Ph-C(3), 22.6 (Ph-C(4)), 33.8 (*t*-Bu)	this work

[a] Values rounded to two decimal places. [b] Values rounded to one decimal place.

Rotation of the allyl ligand by 90° results in loss of this interaction. In the cyclopropenyl analogues **6**, however, each of the degenerate pair of orbitals, **15**, can overlap effectively with a″ on the metal so that the interaction is maintained during cyclopropenyl ligand rotation. If the cyclopropenyl ligand is considered to be $C_3R_3^-$, a four-electron donor, both the allyl complexes and complexes **6** can be considered to be d^4 M(II) compounds, whereas the W(IV) relatives **5** possess a d^2 configuration. Clearly the difference in electronic configuration has a marked effect on the facility of C_3 ring rotation, but it is not clear at present how this effect operates.

The structurally characterized (*tert*-butyldiphenylcyclopropenyl)molybdenum(II) complex **6b** and its tungsten analogue **6c** are close relatives of the puckered (metallacyclobutadiene)tungsten(IV) compound **4a**,[9] differing only in formal oxidation state and in the substitution of Cl for CO ligands. Prior to our determination of the molecular structure of **6b** we thought it possible that the preferred ground-state structure of **4a** might indeed be the η^3-cyclopropenyl form and that deformation to the puckered metallacycle arose from steric repulsion between the *tert*-butyl substituent and the C_5H_5 ring. The observed structure and dynamic behavior of **6b** (and **6c**) make this an implausible hypothesis, since free rotation of the C_3 ring is relatively unimpaired. Apparently, the difference in oxidation state between compounds **4** and **6**, and the presence of Cl or CO ligands, exerts a dramatic influence on the ground-state structure; the nature of these effects await a satisfactory theoretical explanation.

The facile ring expansion of some η^3-cyclopropenyl ligands to give η^3-oxocyclobutenyl compounds also deserves discussion. Oxocyclobutenyl compounds of molybdenum have been characterized previously,[20] and analogous complexes of cobalt,[28] iron,[21-23,31] and manganese[21] have also been prepared and studied. Alternative routes to oxocyclobutenyl complexes of chromium, molybdenum, and tungsten will be discussed in a separate paper.[32] The functionalization of the ring ketone to give alkoxy-[22,33] and methylcyclobutadiene[36] ligands has also proven to be a useful synthetic method. We have shown previously that the immediate precursor to the oxocyclobutenyl ligand must be a (2-cyclopropene-1-carbonyl)metal species **12**, which then undergoes ring expansion.[28] Coordinatively saturated (2-cyclopropene-1-carbonyl)metal complexes, in which the cyclopropene olefin cannot interact with the metal, have been isolated, and do not undergo this ring expansion.[35] Moreover, mere coordination of the cyclopropene olefin to the metal center is not enough to induce ring opening or expansion, since the (2-cyclopropene-1-carboxylato)molybdenum complex **13** is inert to such actions.[34]

The effect of added halide ion on the oxidative addition chemistry leading to cyclopropenyl or oxocyclobutenyl complexes is interesting, and we presume that the putative intermediate **7a** is formed by a halide-induced ring expansion reaction; this reaction has been discussed by others.[20] That ring expansion of an η^3-cyclopropenyl ligand to an oxocyclobutenyl ligand can indeed be induced by exogenous ligands is nicely demonstrated by the thermal reactions of **6a** with tertiary phosphorus ligands to yield compounds **9**. We have made a detailed study of this ring expansion reaction for η^3-cyclopropenyl complexes of iron and these results will be reported in a later paper.[31] It is notable that halide-induced ring expansion is *not* observed in oxidative addition reactions of the *tert*-butyldiphenylcyclopropenyl cation nor can the η^3-*tert*-butyldiphenylcyclopropenyl ligand in complex **6b** be induced to ring expand in the presence of dimethylphenylphosphine, either thermally or photochemically. A similar lack of reactivity of this particular ligand toward ring expansion has also been noted for $[Fe(\eta^3\text{-}C_3Ph_2\text{-}t\text{-}Bu)(CO)_2(NO)]$,[31] and the origins of this inertness are under further investigation.

Experimental Section

General Procedures. Reactions were carried out in conventional oven-dried Schlenck glassware under an atmosphere of dinitrogen which was deoxygenated over BASF catalyst and dried over P_4O_{10} or in a Vacuum Atmospheres glovebox equipped with a HE-493 gas purification system. Hydrocarbon and ethereal solvents were dried by distillation from sodium or potassium benzophenone ketyl. Acetonitrile and methylene chloride were distilled from P_4O_{10}. All solvents were stored and transferred under purified dinitrogen.

The 300-MHz ^1H NMR spectra and 75-MHz $^{13}C\{^1H\}$ NMR spectra were obtained on a Varian XL-300 spectrometer; chemical shifts are reported in parts per million downfield from internal tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer and calibrated against the 1601 cm^{-1} peak of polystyrene. Microanalyses were performed by Spang, Eagle Harbor, MI.

Starting Materials. Ammonium hexafluorophosphate and diphenylacetylene were purchased from Aldrich Chemical Co. and were used without further purification. Hexacarbonylmolybdenum and hexacarbonyltungsten were purchased from Pressure Chemical Co. and were used without purification. Dimethylphenylphosphine was purchased from Strem Chemical Co. and used as purchased. Triphenyl phosphite was purchased from Eastman Kodak Co. and was used without further purification. Cyclopentadienylthallium was purchased from Aldrich and was sublimed before use.

Triphenylcyclopropenyl chloride was prepared according to the method of Breslow.[37]

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(31) Hughes, R. P.; Lambert, J. M. J.; Hubbard, J. L., manuscript in preparation.

(32) Hughes, R. P.; Kläui, W.; Reisch, J. W.; Müller, A., following paper in this issue.

(33) Donaldson, W. A.; Hughes, R. P.; Davis, R. E.; Gadol, S. M. *Organometallics* **1982**, *1*, 812–819.

(34) Hughes, R. P.; Reisch, J. W.; Rheingold, A. L. *Organometallics* **1985**, *4*, 241–244.

(35) Desrosiers, P. J.; DeSimone, D. M.; Hughes, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 4842–4846.

(36) Hughes, R. P.; Reisch, J. W.; Rheingold, A. L. *Organometallics* **1984**, *3*, 1761–1763.

(37) Breslow, R.; Chang, H. W. *J. Am. Chem. Soc.* **1961**, *83*, 2367.

Triphenylcyclopropenyl hexafluorophosphate was prepared from the metathetical reaction of triphenylcyclopropenyl chloride (3.5 g, 11.5 mmol) and ammonium hexafluorophosphate (20.0 g, 123 mmol) in methanol (600 mL). Water (200 mL) was added, and the white crystals were collected by vacuum filtration and washed twice with cold anhydrous diethyl ether (50 mL) to give the product (85%).

***tert*-Butyldiphenylcyclopropenyl hexafluorophosphate** was prepared from *tert*-butylphenylacetylene,[38] by the method of Zimmerman.[39]

(η-Triphenylcyclopropenyl)dicarbonyltris(acetonitrile)molybdenum(1+) Hexafluorophosphate (8). Hexacarbonylmolybdenum (0.61 g, 2.31 mmol) was refluxed in CH_3CN (70 mL) for 4 h. The yellow solution was cooled to ambient temperature, and triphenylcyclopropenyl hexafluorophosphate (0.95 g, 2.30 mmol) was added. The solution was heated to 65 °C overnight and then cooled, and the solvent was removed in vacuo. The residue was crystallized from methylene chloride/ether to give the product (1.02 g, 64%): mp >150 °C dec; IR (KBr) ν_{CN} 2317, 2287, ν_{CO} 1954, 1884 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.62 (m, 15 H, Ph); 2.68 (s, 3 H, CH_3CN), 2.35 (s, 6 H, CH_3CN); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 217.56 (CO), 131.32 (Ph), 130.22 (Ph), 128.44 (Ph), 124.67 (Ph), 45.05 (*C*Ph), 3.69 ($NCCH_3$), 2.96 ($NCCH_3$). Resonances due to the nitrile carbon of CH_3CN were not observed. Anal. Calcd for $C_{29}H_{24}F_6MoN_3O_2P$: C, 50.66; H, 3.49; N, 6.11. Found: C, 51.03; H, 3.62; N, 6.20.

(η-Cyclopentadienyl)(η-triphenylcyclopropenyl)dicarbonylmolybdenum (6a). Complex 8 (0.20 g, 0.29 mmol) was dissolved in THF (20 mL). Cyclopentadienylthallium (0.79 g, 2.9 mmol) was added, and the mixture was stirred at ambient temperature overnight. The product was chromatographed at −20 °C on a Florisil column (25 g) and eluted as an orange band with hexane. Evaporation and crystallization of the residue from hexane yielded the product as orange-red crystals (0.13 g, 93%): mp 143–144 °C dec; IR (hexane) ν_{CO} 1971, 1912 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30 (m, 15 H, Ph); 5.00 (s, 5 H, C_5H_5); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −80 °C) δ 229.53 (CO), 135.38 (Ph), 128.89 (Ph), 128.29 (Ph), 126.24 (Ph), 90.33 (C_5H_5), 34.01 (*C*Ph). Anal. Calcd for $C_{28}H_{20}MoO_2$: C, 69.43; H, 4.16. Found: C, 69.38; H, 4.24. A single crystal was selected for an X-ray diffraction study (see below).

(η-Cyclopentadienyl)(η-*tert*-butyldiphenylcyclopropenyl)dicarbonylmolybdenum (6b). Hexacarbonylmolybdenum (0.44 g, 1.67 mmol) was refluxed in CH_3CN (45 mL) for 4.5 h. The yellow solution was cooled to ambient temperature, and *tert*-butyldiphenylcyclopropenyl hexafluorophosphate (0.658 g, 1.68 mmol) and sodium bromide (0.172 g, 1.67 mmol) were added. The mixture was heated to 65 °C overnight. The resultant orange solution was cooled to ambient temperature, the solvent was removed in vacuo, and dry THF (35 mL) was added. Freshly sublimed cyclopentadienylthallium (0.47 g, 1.74 mmol) was added, and the solution was stirred at ambient temperature overnight. Florisil (3 g) was added, and the solvent was removed in vacuo. The coated Florisil was added to the top of a Florisil column (25 g) prepared in hexane. The orange product eluted with hexane and was recrystallized from hexane to give orange-red crystals (0.39 g, 50%): mp 110–112 °C dec; IR (hexane) ν_{CO} 1978, 1915 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (m, 10 H, Ph), 4.90 (s, 5 H, Cp), 1.10 (s, 9 H, *t*-Bu); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −80 °C) δ 231.81 (MoCO), 137.49 (Ph), 129.50 (Ph), 128.76 (Ph), 126.14 (Ph), 90.42 (C_5H_5), 52.64 (*C*Ph), 33.62 ($CCMe_3$), 33.16 (CMe_3), 31.80 (CMe_3). Anal. Calcd for $C_{26}H_{24}MoO_2$: C, 67.24; H, 5.21. Found: C, 67.67; H, 5.47. A single crystal was selected for an X-ray diffraction study (see below).

(η-Cyclopentadienyl)(η-*tert*-butyldiphenylcyclopropenyl)dicarbonyltungsten (6c). Hexacarbonyltungsten (1.02 g, 2.90 mmol) was refluxed in acetonitrile (75 mL) for 1 week. The yellow solution was cooled to ambient temperature and filtered through filter cel, and the filter cel was washed with acetonitrile (10 mL). *tert*-Butyldiphenylcyclopropenyl hexafluorophosphate (1.12 g, 2.85 mmol) and sodium bromide (0.298 g, 2.90 mmol) were added, and the solution quickly turned red. The mixture was heated to 80 °C for 48 h. The resultant red solution was cooled to ambient temperature, and the solvent was removed in vacuo. Dry THF (70 mL) and cyclopentadienylthallium (0.783 g, 2.91 mmol) were added, and the mixture was stirred overnight. Degassed Florisil (3 g) was added, and the solvent was removed in vacuo. The coated Florisil was added to the top of a Florisil column (2.5 × 25 cm) prepared in hexane. An orange band eluted with hexane and was evaporated to yield an orange solid which was crystallized from hexane to give the product as orange crystals (0.35 g, 22%): mp >100 °C dec; IR (hexane) ν_{CO} 1971, 1906 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32 (m, 10 H, Ph), 5.03 (s, 5 H, Cp), 1.24 (s, 9 H, *t*-Bu); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −80 °C) δ 220.39 (WCO), 137.43 (Ph), 130.10 (Ph), 129.15 (Ph), 128.33 (Ph), 125.26 (Ph), 88.01 (C_5H_5), 44.78 (*C*Ph), 32.36 (CMe_3), 31.28 (CMe_3), 21.43 ($CCMe_3$). Anal. Calcd for $C_{26}H_{24}O_2W$: C, 56.52; H, 4.35. Found: C, 56.65; H, 4.45.

(η-Cyclopentadienyl)(η^3-triphenyloxocyclobutenyl)dicarbonylmolybdenum(II) (9a). Hexacarbonylmolybdenum (3.39 g, 12.8 mmol) was refluxed in acetonitrile (75 mL) for 4 h. The yellow solution was cooled to ambient temperature, and triphenylcyclopropenyl hexafluorophosphate (5.30 g, 12.8 mmol) and sodium bromide (1.30 g, 12.6 mmol) were added. The mixture was heated to 80 °C overnight and then cooled to room temperature, and the solvent was removed in vacuo. Dry THF (75 mL) and cyclopentadienylthallium (3.47 g, 12.9 mmol) were added, and the solution was stirred at ambient temperature overnight. Florisil (4 g) was added, and the solvent was removed in vacuo. The coated Florisil was added to the top of a Florisil column (3 × 30 cm) prepared in hexane. The yellow product eluted with ether and was crystallized from methylene chloride/hexane to give yellow crystals (4.0 g, 61%): mp 205–206 °C dec; IR (CH_2Cl_2) ν_{CO} 2001, 1945, $\nu_{C=O}$ 1677 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36 (m, 15 H, Ph), 5.20 (s, 5 H, C_5H_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 227.78 (CO), 168.33 (C=O), 135.54 (Ph), 132.53 (Ph), 131.00 (Ph), 128.52 (Ph), 127.99 (Ph), 125.84 (Ph), 90.20 (C_5H_5), 89.36 (*C*Ph), 70.12 (*C*Ph). Anal. Calcd for $C_{29}H_{20}MoO_3$: C, 67.98; H, 3.93. Found: C, 67.57; H, 4.18.

(η-Cyclopentadienyl)(η^3-triphenyloxocyclobutenyl)dicarbonyltungsten(II) (9b). Hexacarbonyltungsten (2.12 g, 6.03 mmol) was refluxed in acetonitrile (75 mL) for 3 days. Triphenylcyclopropenyl hexafluorophosphate (2.48 g, 6.02 mmol) and sodium bromide (0.62 g, 6.02 mmol) were added, and the solution was heated to 80 °C overnight. After cooling and removal of the solvent in vacuo, dry THF (75 mL) and cyclopentadienylthallium (1.62 g, 6.01 mmol) were added and the mixture was stirred overnight. Florisil (4 g) was added, and the solvent was removed in vacuo. The coated Florisil was added to the top of a Florisil column (2.5 × 25 cm) prepared in hexane. A pale orange band eluted with ether and was evaporated in vacuo. The residue was crystallized from CH_2Cl_2/hexane to give pale orange crystals (1.22 g, 34%): mp 206–209 °C dec; IR (CH_2Cl_2) ν_{CO} 1995, 1943, $\nu_{C=O}$ 1677 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38 (m, 15 H, Ph), 5.21 (s, 5 H, C_5H_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 214.79 (WCO), 170.36 (C=O), 136.07 (Ph), 132.09 (Ph), 128.73 (Ph), 127.99 (Ph), 125.68 (Ph), 92.97 (C_5H_5), 81.57 (*C*Ph), 60.67 (*C*Ph). Anal. Calcd for $C_{29}H_{20}O_3W$: C, 58.02; H, 3.35. Found: C, 57.94; H, 3.44.

(η-Cyclopentadienyl)(η^3-triphenyloxocyclobutenyl)(dimethylphenylphosphine)carbonylmolybdenum(II) (11a). (η-Cyclopentadienyl)(η^3-triphenylcyclopropenyl)dicarbonylmolybdenum (6a) (0.44 g, 0.91 mmol) was dissolved in dry CH_3CN (25 mL). Dimethylphenylphosphine (130 μL, 0.94 mmol) was added, and the solution was heated to 75 °C for 2 h and then cooled to room temperature. Florisil (4 g) was added, the solvent was removed in vacuo, and the coated Florisil was added to the top of a Florisil column (2.5 × 25 cm) prepared in hexane. The product was eluted with ether and crystallized from CH_2Cl_2/hexane to give yellow crystals (0.26 g, 46%): mp 205–210 °C dec; IR (CH_2Cl_2) ν_{CO} 1896, $\nu_{C=O}$ 1651 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1–7.9

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(41) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(m, Ph), 4.72 (d, J_{PH} = 1.8 Hz, C_5H_5), 1.57 (d, J_{PH} = 8.5 Hz, PMe), 0.97 (d, J_{PH} = 8.5 Hz, PMe). Anal. Calcd for $C_{36}H_{31}MoO_2P$: C, 69.45; H, 5.02. Found: C, 69.39; H, 5.03.

(η-Cyclopentadienyl)(η^3-triphenyloxocyclobutenyl)carbonyl(triphenyl phosphite)molybdenum(II) (11b). (η-Cyclopentadienyl)(η^3-triphenylcyclopropenyl)dicarbonylmolybdenum (**6a**) (0.15 g, 0.31 mmol) was dissolved in benzene (30 mL). Triphenyl phosphite (100 μL, 0.38 mmol) was added, and the solution was heated to reflux overnight and then cooled to room temperature. Florisil (4 g) was added, and the solvent was removed in vacuo. The coated Florisil was added to the top of a Florisil column prepared in hexane. The product eluted with 50:50 methylene chloride/ether and was crystallized from CH_2Cl_2/hexane to give yellow crystals (0.11 g, 45%): mp 195–201 °C dec; IR (CH_2Cl_2 ν_{CO} 1933, $\nu_{C=O}$ 1663 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–6.5 (m, 30 H, Ph), 4.67 (d, J_{PH} = 1.1 Hz, C_5H_5). Anal. Calcd for $C_{46}H_{35}MoO_5P$: C, 69.52; H, 4.44. Found: C, 69.32; H, 4.77.

X-ray Diffraction Studies. Crystalline samples of **6a** and **6b** of a quality suitable for diffraction studies were obtained by recrystallization from CH_2Cl_2/hexane at −30 °C. Unit-cell parameters, as reported in Table I, were obtained from angular settings of 25 reflections (20° ≤ 2θ ≤ 30°) containing Friedel related reflections to judge optical alignment. Systematic absences uniquely defined the space groups of **6a** and **6b**. During data reduction corrections were made for decay and *Lp* effects, but none for absorption were required.

Standard heavy-atom methods were used to locate the Mo atom in both **6a** and **6b**, and the remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. In the final cycles of blocked-cascade refinement, all non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were placed in idealized, updated locations (d(C–H) = 0.96 Å, U = 1.2 × attached carbon U). Additionally, in **6a** the three phenyl rings were treated as rigid, planar rings (d(C–C) = 1.395 Å).

Atomic coordinates for **6a** and **6b** are provided in Tables II and III, respectively. Selected bond distances and angles are given in Table IV. Additional crystallographic data are available as supplementary material.[29]

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Registry No. **6a**, 82661-45-8; **6b**, 97689-46-8; **6c**, 97689-44-6; **8**, 97689-41-3; **9a**, 82661-46-9; **9b**, 92144-96-2; **11a**, 82661-47-0; **11b**, 97689-45-7; $W(CO)_6$, 14040-11-0; $Mo(CO)_6$, 13939-06-5; cyclopentadienylthallium, 34822-90-7; triphenylcyclopropenyl hexafluorophosphate, 42134-08-7; triphenylcyclopropenyl chloride, 58090-78-1; ammonium hexafluorophosphate, 16941-11-0; *tert*-butyldiphenylcyclopropenyl hexafluorophosphate, 97689-43-5.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, fractional coordinates and isotropic thermal parameters for the hydrogen atoms, anisotropic thermal parameters, and bond distances and angles for **6a** (Tables 1S–5S) and **6b** (Tables 6S–10S) (41 pages). Ordering information is given on any current masthead page.

Reactions of Cyclopropenyl Cations with Group 6 Metal Carbonyl Anions. Synthesis of η^3-Oxocyclobutenyl Complexes of Chromium, Molybdenum, and Tungsten[†]

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Reactions of $Na[M(C_5H_5)(CO)_3]$ (M = Mo, W) with the triphenylcyclopropenyl cation lead to apparent redox chemistry, affording the dinuclear compounds $[M(C_5H_5)(CO)_3]_2$ as the only organometallic products. In contrast reactions of the pentamethylcyclopentadienyl analogues $Na[M(C_5Me_5)(CO)_3]$ (M = Cr, Mo, W) with symmetrically substituted cyclopropenyl cations lead to oxocyclobutenyl complexes **4**; unsymmetrically substituted cyclopropenyl cations give exclusively complexes **5**, containing unsymmetrically substituted oxocyclobutenyl ligands. Similarly the molybdenum anion $[MoL(CO)_3]^-$ (L = $[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$) reacts with the triphenylcyclopropenyl cation to give the oxocyclobutenyl complex **6**. Spectroscopic properties of the oxocyclobutenyl complexes and reaction mechanisms are discussed.

Introduction

The reactions of cyclopropenyl cations, or their equivalents, with transition-metal centers have been investigated for a number of years and have been shown to give rise to a variety of products. The three-membered ring may be maintained intact in the form of 3-η^1-,[3-6] η^2-[7-9] or η^3-cyclopropenyl ligands,[10-22] or ring cleavage may occur to

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[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III→3 and 13.)

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