Cyclopropenyl and Oxocyclobutenyl Complexes of Molybdenum. Crystal and Molecular Structures of (2,2'-Bipyridine)bromodicarbonyl(1—3-η-1,2,3-triphenylcyclopropenyl)molybdenum(II) and (2,2'-Bipyridine)bromodicarbonyl(2—4-η-1-oxo-2,3,4-triphenylcyclobutenyl)molybdenum(II)

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Reactions of triphenylcyclopropenyl bromide with $[\mathrm{Mo(CO)_4L_2}]$ [L_2 = 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), or 2,2'-dipyridylamine (dpa)] yield the two series of products $[\mathrm{MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)L_2}]$ and $[\mathrm{MoBr(CO)_2(\eta^3\text{-}C_4Ph_3O)L_2}]$. The cyclopropenyl complexes were also prepared from $[\mathrm{MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)(NCMe)_2}]$ by reaction with L_2 in MeCN, which yielded crystalline solvates suitable for an *X*-ray structure determination. Crystals of $[\mathrm{MoBr(CO)_2(\eta^3\text{-}C_4Ph_3O)(bipy)}]$·thf, (1), are monoclinic, $a = 9.87(1)$, $b = 20.36(1)$, $c = 16.23(1)$ Å, $\beta = 92.2(1)°$, $Z = 4$, space group $P2_1/c$. Crystals of $[\mathrm{MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)(bipy)}]$·MeCN, (2), are triclinic, $a = 10.552(8)$, $b = 11.607(9)$, $c = 13.801(11)$ Å, $\alpha = 67.1(1)$, $\beta = 100.4(1)$, $\gamma = 89.5(1)°$, $Z = 2$, space group $P\bar{1}$. 2 832 and 1 804 above background reflections were collected on a diffractometer and refined by full-matrix least squares to *R* 0.072 and 0.082 for (1) and (2) respectively. In both structures the molybdenum atoms are in octahedral environments, with the mutually *cis* carbonyl groups and the bipy ligand occupying an equatorial plane. In *trans* positions are a bromine atom and in (1) a η^3-oxocyclobutenyl group and in (2) a η^3-cyclopropenyl group.

THE zerovalent molybdenum complexes $[\mathrm{Mo(CO)_n[L_{6-n}]}]$ [$n = 3$, L = MeCN; $n = 4$, L_2 = 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), or 2,2'-dipyridylamine (dpa)] and the anions $[\mathrm{MoX(CO)_3L_2}]^-$ (X = halide) readily undergo oxidative addition reactions with allylic halides to give η^3-allyl complexes $[\mathrm{MoX(CO)_2(\eta^3\text{-}allyl)(NCMe)_2}]$ [1] and $[\mathrm{MoX(CO)_2(\eta^3\text{-}allyl)L_2}]$.[2-4] It was therefore of interest to treat these same carbonyl derivatives with other organic substrates which were capable of yielding η^3-bonded products, but which were more sensitive to the nucleophilicity of the metal complex. We chose triphenylcyclopropenyl bromide as such a reactant in view of the wide range of products formed in the reactions of triarylcyclopropenyl derivatives with other low-valent transition-metal complexes,[5-10] and here we report details of these reactions together with single-crystal *X*-ray diffraction studies of two of the products.

EXPERIMENTAL

All preparations were performed in an atmosphere of dry N_2 gas using solvents and liquid reagents freed from moisture and oxygen by standard procedures. The starting materials $\mathrm{C_3Ph_3Br}$, $[\mathrm{Mo(CO)_4L_2}]$ and $[\mathrm{PPh_4}][\mathrm{MoBr(CO)_3L_2}]$ (L_2 = bipy, phen, or dpa) were prepared by literature methods.[3,4,11]

Infrared spectra in the region 200—4 000 cm^{-1} were recorded on a Perkin-Elmer 597 spectrophotometer. Hydrogen-1 and ^{13}C n.m.r. spectra were recorded on JEOL PS 100 and FX 90Q FT instruments respectively using $\mathrm{SiMe_4}$ as internal standard; spectroscopic data are in Table 1.

Synthesis of $[\mathrm{MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)(NCMe)_2}]$.—$[\mathrm{Mo(CO)_6}]$ (2.64 g, 10 mmol) was heated under reflux with MeCN (100 cm^3) for 4 h. The solution was treated with $\mathrm{C_3Ph_3Br}$ (3.37 g, 10 mmol) at room temperature, and then evaporated to 20 cm^3 under a stream of N_2 gas. On standing for several days at 10 °C, the product precipitated as a yellow powder.

Synthesis of $[\mathrm{MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)L_2}]$·MeCN [$L_2$ = bipy (2), phen (4), or dpa (6)].—A solution of $[\mathrm{MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)(NCMe)_2}]$ was prepared as above, cooled to −10 °C with stirring, and treated with the ligand L_2 (10 mmol). On standing at this temperature crystals of the products formed and were collected, washed with MeCN, and dried *in vacuo*.

Synthesis of $[\mathrm{MoBr(CO)_2(\eta^3\text{-}C_4Ph_3O)L_2}]$·thf [$L_2$ = bipy (1), phen (3), or dpa (5)].—$[\mathrm{Mo(CO)_4L_2}]$ (2 mmol) and $\mathrm{C_3Ph_3Br}$ (0.67 g, 2 mmol) were allowed to react in refluxing tetrahydrofuran (thf) for 4 h. Impure $[\mathrm{MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)L_2}]$ was filtered off, the filtrate evaporated to low bulk (*ca.* 10 cm^3), and the product allowed to crystallise at 10 °C. The adducts could be recrystallised from thf without change, but recrystallisation from solvents of low donicity yielded unsolvated products.

Crystal Data.—(1) $[\mathrm{MoBr(CO)_2(\eta^3\text{-}C_4Ph_3O)(bipy)}]$·thf, $\mathrm{C_{38}H_{31}BrMoN_2O_4}$, $M = 755.1$, Monoclinic, $a = 9.87(1)$, $b = 20.36(1)$, $c = 16.23(1)$ Å, $\beta = 92.2(1)°$, $U = 3\,259.1$ Å^3, $F(000) = 1\,532$, $D_m = 1.55$ g cm^{-3}, $Z = 4$, $D_c = 1.54$, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 17.4$ cm^{-1}, space group $P2_1/c$ from the systematic absences $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$.

(2) $[\mathrm{MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)(bipy)}]$·MeCN, $\mathrm{C_{35}H_{26}BrMoN_2O_2}$, $M = 696.1$, Triclinic, $a = 10.552(8)$, $b = 11.607(9)$, $c = 13.801(11)$ Å, $\alpha = 67.1(1)$, $\beta = 100.4(1)$, $\gamma = 89.5(1)°$, $U = 1\,525.4$ Å^3, $D_m = 1.50$ g cm^{-3}, $Z = 2$, $D_c = 1.51$, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 18.6$ cm^{-1}, $F(000) = 700$, space group $P\bar{1}$ from the successful structure determination.

Both crystals were set up to rotate around the *a* axis on a Stoe STADI-2 diffractometer. Their approximate sizes were 0.4 × 0.3 × 0.3 and 0.5 × 0.2 × 0.2 mm respectively. Data were collected *via* an ω scan [speed 30 s degree^{-1}, background time 20 s, scan width $(1.5 + 0.5 \sin\mu/\tan\theta)$]. For (1) 4 398 reflections with $2\theta_{\max.}$ of 45° were collected, and for (2) 2 909 reflections with $2\theta_{\max.}$ of 40°. Data were not corrected for absorption or extinction. For (1) 2 832 and for (2) 1 804 independent reflections with $I > 2\sigma(I)$ were used in subsequent calculations.

Structure Determination.—The positions of the molybdenum and bromine atoms were obtained from the Patterson function. Subsequent Fourier maps enabled the remaining non-hydrogen atoms to be located. For (1), hydrogen atoms were placed in trigonal positions on the bipy and

TABLE 1

Analytical data (calculated values in parentheses) and selected i.r. data

	Analyses (%)			Yields	Carbonyl i.r. data [a]			Force constants ($\times 10^3$)/N m^{-1} [b]	
Compound	C	H	N	(%)	A′	A″	C_4Ph_3O	k	k_i
(1) $[MoBr(CO)_2(\eta^3\text{-}C_4Ph_3O)(bipy)]\cdot thf$	60.1	4.1	4.0	37	1 998	1 930	1 640	15.6	0.54
	(60.4)	(4.1)	(3.7)						
(2) $[MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)(bipy)]\cdot MeCN$	58.8	3.5	6.0	68	1 950	1 880		14.8 [c]	0.53
	(60.3)	(3.8)	(6.0)		1 936	1 868			
(3) $[MoBr(CO)_2(\eta^3\text{-}C_4Ph_3O)(phen)]\cdot thf$	62.1	4.5	3.8	36	1 995	1 932	1 660	15.6	0.50
	(61.6)	(4.0)	(3.6)						
(4) $[MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)(phen)]\cdot MeCN$ [d]	61.4	3.7	5.6	74	1 938	1 866		14.6 [c]	0.55
	(61.7)	(3.6)	(5.8)		1 948				
(5) $[MoBr(CO)_2(\eta^3\text{-}C_4Ph_3O)(dpa)]\cdot thf$	59.4	4.4	5.3	28	1 990	1 918	1 640	15.4	0.57
	(59.3)	(4.0)	(5.5)						
(6) $[MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)(dpa)]\cdot MeCN$ [d]	59.6	4.0	7.6	30	1 932	1 860		14.5	0.55
	(59.1)	(3.8)	(7.9)						
(7) $[MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)(NCMe)_2]$	55.4	3.8	5.0	30	1 958	1 892		15.0	0.51
	(56.7)	(3.7)	(4.9)						

[a] Recorded on Nujol mulls (cm^{-1}). [b] Calculated by the method given in F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, 1962, **84**, 4432. [c] Calculated from the average position of split bands. [d] MeCN readily lost leading to low N analyses for some samples.

phenyl rings. They were given fixed thermal parameters equivalent to those of the atom to which they were bonded. The other atoms were refined anisotropically and the final R was 0.072.

For (2) the phenyl rings were defined as rigid groups with hydrogen atoms in the appropriate positions. Hydrogen atoms in the bipy ligand were positioned in trigonal sites. Their thermal parameters were fixed as in (1). All atoms were refined anisotropically to R 0.082. Calculations were done using the SHELX 76 package [12] at the University of Manchester Computer Centre. Scattering factors and dispersion corrections were taken from ref. 13. In the final cycles of refinement no shift was greater than 0.2σ. The two structures had the same weighting scheme $w^{\frac{1}{2}} = 1/[\sigma^2(F) + 0.003F^2]$ where $\sigma(F)$ was obtained from counting statistics. This gave similar values of $w\Delta^2$ over ranges of F_o and $(\sin\theta)/\lambda$. Difference Fouriers showed no significant regions of electron density. Positional parameters for (1) and (2) are given in Tables 2 and 3. Thermal parameters, hydrogen atom positions, and structure factors are given in Supplementary Publication No. SUP 23031 (51 pp.).*

RESULTS AND DISCUSSION

It has been noted previously that the reaction of triarylcyclopropenyl compounds with metal carbonylate anions does not generally yield η^3-cyclopropenyl complexes,[6] and instead η^3-oxocyclobutenyl,[14] metallacyclobutenyl,[9] and σ-cyclopropenyl complexes [10] have resulted. No analogous products could be detected in the reaction of the anions $[MoBr(CO)_3L_2]^-$ with C_3Ph_3Br: even when the reaction was carried out at −20 °C only non-carbonyl containing products were formed. However, cyclopropenyl complexes were isolated by the route shown in equation (1), although attempts to

$$[Mo(CO)_6] \xrightarrow{MeCN} [Mo(CO)_3(NCMe)_3] \xrightarrow{C_3Ph_3Br} [MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)(NCMe)_2] \xrightarrow{L_2} [MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)L_2] + 2MeCN \qquad (1)$$

prepare a larger range of complexes containing mono- and bi-dentate Group 5 donor ligands by replacement of MeCN in $[MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)(NCMe)_2]$, (7), in an analogous manner to that used for the corresponding η^3-allyl complexes,[1,15] generally resulted in low yields of

TABLE 2

Atomic co-ordinates for (1) ($\times 10^4$) with estimated standard deviations in parentheses

Atom	X	Y	Z
Mo	1 092(1)	1 107(0)	2 540(1)
Br	−965(1)	666(1)	1 634(1)
C(7)	2 105(10)	871(6)	1 546(7)
O(7)	2 650(9)	711(5)	959(5)
C(8)	462(11)	1 920(6)	1 941(7)
O(8)	13(9)	2 353(4)	1 587(6)
N(52)	969(8)	107(4)	3 062(6)
N(62)	−489(8)	1 152(5)	3 486(5)
C(51)	−11(11)	9(6)	3 626(7)
C(53)	1 643(13)	−420(6)	2 812(9)
C(54)	1 454(13)	−1 051(6)	3 112(9)
C(55)	500(16)	−1 140(7)	3 702(9)
C(56)	−209(14)	−620(7)	3 964(8)
C(61)	−787(11)	580(6)	3 852(7)
C(63)	−1 206(11)	1 695(7)	3 639(7)
C(64)	−2 272(11)	1 686(8)	4 162(8)
C(65)	−2 647(12)	1 094(8)	4 515(8)
C(66)	−1 883(12)	539(7)	4 360(8)
C(1)	3 043(10)	1 649(5)	2 747(6)
C(2)	2 133(10)	1 894(5)	3 392(6)
C(3)	3 231(10)	1 041(5)	3 207(6)
C(4)	2 455(10)	1 307(5)	3 893(7)
O(4)	2 201(7)	1 119(4)	4 598(4)
C(11)	3 969(10)	1 995(5)	2 195(6)
C(12)	5 338(12)	2 035(7)	2 442(9)
C(13)	6 244(14)	2 358(8)	1 973(10)
C(14)	5 855(13)	2 680(7)	1 267(9)
C(15)	4 498(14)	2 646(7)	1 006(9)
C(16)	3 576(13)	2 305(6)	1 459(8)
C(21)	1 686(9)	2 550(5)	3 615(7)
C(22)	1 195(11)	2 652(6)	4 394(7)
C(23)	801(13)	3 272(6)	4 651(7)
C(24)	854(13)	3 794(6)	4 118(8)
C(25)	1 360(10)	3 709(6)	3 343(7)
C(26)	1 738(10)	3 096(6)	3 098(7)
C(31)	4 204(10)	486(6)	3 177(7)
C(32)	5 017(11)	392(6)	2 507(8)
C(33)	5 934(10)	−129(6)	2 527(8)
C(34)	6 021(11)	−568(6)	3 186(9)
C(35)	5 220(11)	−462(6)	3 856(8)
C(36)	4 304(11)	65(6)	3 852(8)
O(100)	6 617(15)	3 259(8)	4 066(11)
C(101)	5 256(20)	3 444(11)	3 920(14)
C(102)	7 117(21)	3 711(12)	4 626(15)
C(103)	6 057(22)	4 081(12)	5 009(15)
C(104)	4 963(21)	3 954(13)	4 441(15)

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

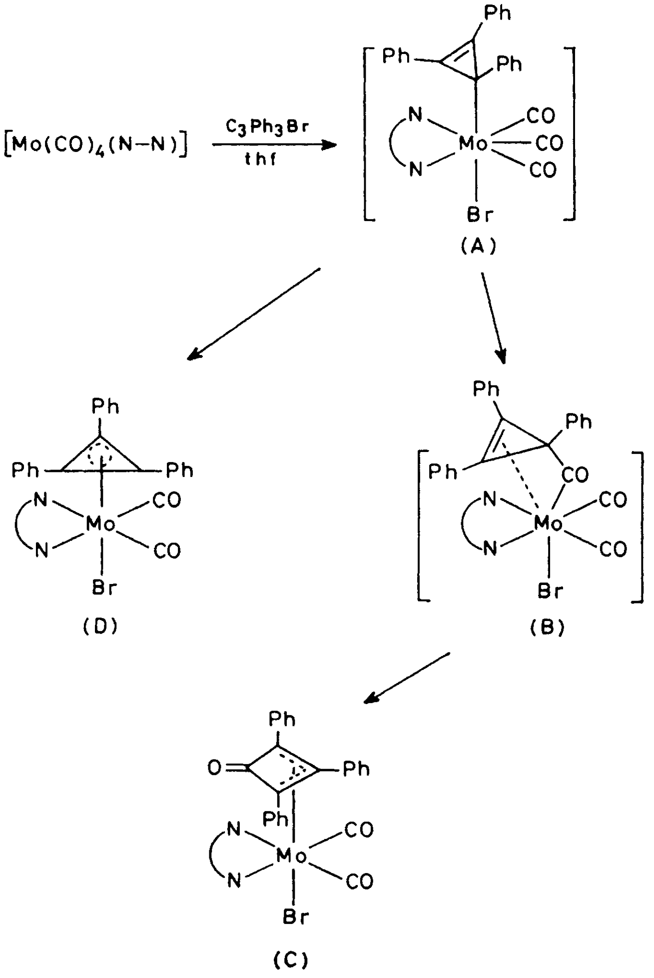
TABLE 3

Atomic co-ordinates for (2) (× 10^4) with estimated standard deviations in parentheses

Atom	X	Y	Z
Mo(1)	2 471(2)	2 488(2)	772(2)
Br(1)	2 271(2)	2 770(2)	−1 234(2)
C(7)	593(23)	3 054(21)	389(19)
O(7)	−445(13)	3 452(16)	25(13)
C(8)	2 905(20)	4 265(23)	244(20)
O(8)	3 165(14)	5 278(15)	−50(14)
N(52)	2 202(18)	488(16)	1 076(13)
N(62)	4 439(15)	1 639(18)	949(13)
C(51)	3 285(21)	−215(19)	1 222(17)
C(53)	1 060(20)	−76(23)	1 160(17)
C(54)	999(33)	−1 327(29)	1 311(19)
C(55)	2 095(33)	−2 040(29)	1 440(20)
C(56)	3 252(29)	−1 516(25)	1 401(17)
C(61)	4 570(22)	356(20)	1 188(15)
C(63)	5 477(17)	2 295(17)	890(14)
C(64)	6 717(19)	1 650(23)	1 111(18)
C(65)	6 848(23)	409(28)	1 313(20)
C(66)	5 723(23)	−257(22)	1 369(18)
C(1)	3 012(19)	1 624(19)	2 530(15)
C(2)	2 982(19)	2 941(19)	2 196(17)
C(3)	1 774(15)	2 346(19)	2 269(15)
C(11)	3 780(13)	463(11)	3 264(11)
C(12)	3 219(13)	−674(11)	3 619(11)
C(13)	3 987(13)	−1 782(11)	4 280(11)
C(14)	5 317(13)	−1 754(11)	4 588(11)
C(15)	5 878(13)	−617(11)	4 233(11)
C(16)	5 110(13)	491(11)	3 571(11)
C(21)	3 576(13)	3 893(12)	2 577(11)
C(22)	2 920(13)	4 441(12)	3 104(11)
C(23)	3 536(13)	5 243(12)	3 536(11)
C(24)	4 808(13)	5 496(12)	3 441(11)
C(25)	5 464(13)	4 948(12)	2 914(11)
C(26)	4 848(13)	4 147(12)	2 483(11)
C(31)	574(11)	2 355(14)	2 619(12)
C(32)	196(11)	1 264(14)	3 354(12)
C(33)	−909(11)	1 316(14)	3 763(12)
C(34)	−1 637(11)	2 459(14)	3 436(12)
C(35)	−1 259(11)	3 551(14)	2 701(12)
C(36)	−154(11)	3 499(14)	2 293(12)
N(100)	−763(61)	3 415(55)	−4 226(46)
C(101)	242(81)	2 989(66)	−4 165(54)
C(102)	1 382(71)	3 061(60)	−4 281(49)

insoluble, impure products. Analytical and selected spectroscopic data for the four pure cyclopropenyl products isolated are given in Table 1. The parent complex (7) was extremely air-sensitive in solution and readily decomposed on standing at room temperature, whereas the solvated complexes (2), (4), and (6) were completely stable in the solid state but had extremely low solubilities in all common solvents so preventing their full spectral characterisation. The mass spectra of the complexes yielded no further structural information, only the fragmentation pattern of the cyclopropenyl ligand and the nitrogen bases being observed. Consequently an X-ray study of complex (2) was undertaken, the result of which will be described later in the paper.

Direct reaction of triphenylcyclopropenyl bromide with $[Mo(CO)_4L_2]$ in refluxing thf also resulted in the precipitation of unsolvated but slightly impure cyclopropenyl complexes (2), (4), and (6), in yields of approximately 45, 40, and 55% respectively. Attempts to purify these complexes by recrystallisation were thwarted by the very low solubilities in organic solvents of both the desired products and the contaminants. However, partial evaporation of the filtrate from these reactions resulted in the isolation of the new complexes $[MoBr(CO)_2(\eta^3\text{-}C_4Ph_3O)L_2]\cdot$thf [$L_2$ = bipy (1), phen (3), or dpa (5)] (Table 1). Recrystallisation of these products from solvents of low donicity resulted in loss of thf, and the spectroscopic data on the non-solvated species were as expected for η^3-oxocyclobutenyl complexes with a pseudo-octahedral structure of local C_s symmetry (C), see Scheme [(N–N) represents a bidentate N-donor ligand], similar to that found for the closely related η^3-allyl complex $[Mo(NCS)(CO)_2(\eta^3\text{-}C_3H_5)(bipy)]$.[16] Thus for $[MoBr(CO)_2(\eta^3\text{-}C_4Ph_3O)(bipy)]$ the two carbonyl bands of approximately equal intensities indicated a *cis* arrangement of the carbonyl ligands and ν(CO) of the carbocyclic ligand at 1 680 cm^{-1} was typical of a metal-bonded η^3-oxocyclobutenyl group.[14,17-19] The ^1H n.m.r. spectrum showed three signals for the bipy ligand [8.19 (d, 2 H), 7.88 (m, 4 H), and 7.62 p.p.m. (m, 2 H)] and two for the C_4Ph_3O moiety (7.04 and 7.45 p.p.m.), and only one signal (222.2 p.p.m.) was found for the ligated carbonyl groups in the ^{13}C n.m.r. spectrum.



SCHEME

Spectroscopic data on the solid thf adducts (1), (3), and (5) did not allow us to differentiate unequivocally between a simple solvated η^3-oxocyclobutenyl complex of type (C) or an acyl derivative such as (B) in which the 18-electron configuration of the metal was achieved by co-ordination of either thf or the olefinic linkage in the carbocyclic ligand. The CO stretches of the C_4Ph_3O ligand were 25—50 cm^{-1} lower than that found in the other η^3-oxocyclobutenyl complexes and more typical of acyl bonding.[14,17-19] Furthermore, the ring stretching and breathing vibrations of the thf molecule in the complexes [at 1 050 and 880 cm^{-1} in complex (1), for example] fell between those values generally quoted for free (1 067 and 908 cm^{-1}) and co-ordinated thf (1 020—1 040 and 860—870 cm^{-1}).[20,21] Although n.m.r. measurements showed that thf was liberated on dissolution and spectra otherwise identical to those of the unsolvated complexes resulted, this could have reflected a solvent induced change from (B) to (C), so a single-crystal *X*-ray study of (1) was carried out which revealed that the product was simply a solvated η^3-oxocyclobutenyl complex. Cotton–Kraihanzel force-constant calculations from data measured on the solid complexes (Table 1) show that the C–O stretching force constants (*k*) increase in the series C_3H_5 ($k = 14.4 \times 10^2$ N m^{-1}) $<C_3Ph_3$ ($k = 14.8 \times 10^2$ N m^{-1}) $<C_4Ph_3O$ ($k = 15.6 \times 10^2$ N m^{-1}) when all three ligands are η^3-bonded to the $MoBr(CO)_2$(bipy) moiety, so indicating that the cyclobutenyl ligand is best able to relieve the build up of electron density on the metal atom.

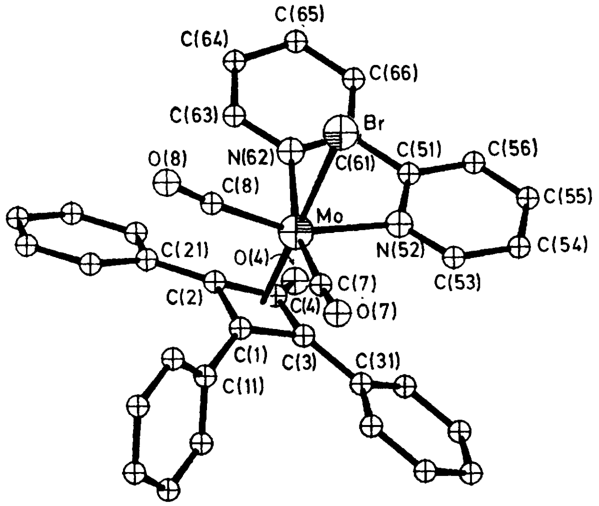


FIGURE 1 Structure of (1) $[MoBr(CO)_2(\eta^3\text{-}C_4Ph_3O)(bipy)]$

Although we were unable to isolate a σ-bonded intermediate of type (A) or (B), both σ-C_3Ph_3 [10] and σ-C(O)-$C_3H_3Ph_3$ [22] species have been characterised in reactions of cyclopropenyl derivatives with other carbonyl complexes so supporting the ring expansion mechanism proposed by Green and co-workers [23] on which our reaction sequence is based. In addition, isolation of both η^3-cyclopropenyl and η^3-oxocyclobutenyl complexes (which are not readily interconverted) from the same reaction gives additional support for the intermediacy of a σ-bonded derivative such as (A) which can react in either of two ways to give the products described above.

Solid-state Structure.—The structures of (1) and (2) together with their common atomic numbering scheme are shown in Figures 1 and 2. The two molecules have very similar structures with the metal atoms in distorted octahedral environments. The positions of the atoms in the $MoBr(CO)_2$(bipy) moieties are equivalent, with the five metal–ligand bonds occupying five sites of the octahedron with the mutually *cis* carbonyl groups *trans* to the bipy nitrogen atoms. In (1) there is a η^3-oxocyclobutenyl group *trans* to the bromine atom in the axial position while in (2) there is a η^3-cyclopropenyl group in this site. These two groups occupy just one

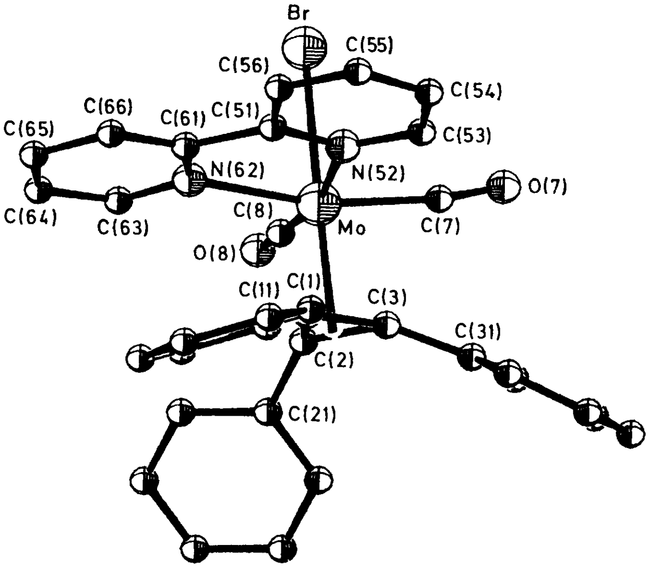


FIGURE 2 Structure of (2) $[MoBr(CO)_2(\eta^3\text{-}C_3Ph_3)(bipy)]$

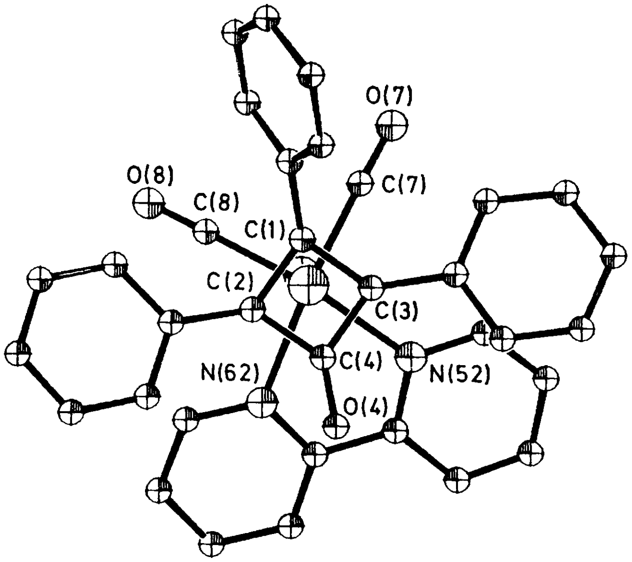


FIGURE 3 The projection of (1) onto the cyclobutenyl plane

site with the centres (C_0) of the four- and three-membered rings exactly *trans* to the bromine atom (C_0–Mo–Br 178.0 and 178.5° respectively). In both (1) and (2) there is a solvent molecule in the asymmetric unit [thf in (1) and MeCN in (2)] but there are no close contacts between it and other molecules.

The Mo–Br [2.619(1); 2.626(3) Å], Mo–C [1.990(11), 2.005(12); 1.992(24), 1.990(25) Å], and Mo–N [2.211(8), 2.233(8); 2.223(19), 2.221(17) Å] distances are equivalent in both (1) and (2) and are typical bond lengths for molybdenum(II) structures.[24] The angles subtended at the metal are however different because of the effect of the oxocyclobutenyl and cyclopropenyl groups. To show the disposition of these two groups in (1) and (2), Figures 3 and 4 are projections of the molecules onto the oxocyclobutenyl and cyclopropenyl planes respectively. In both molecules the rings are arranged to maximise nonbonded contacts and as a result the immediate metal coordination spheres have approximate C_s symmetry.

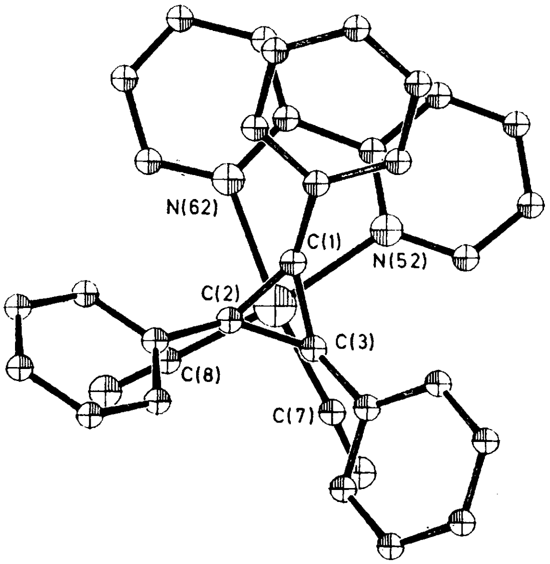


FIGURE 4 The projection of (2) onto the cyclopropenyl plane

As shown in Figure 3, in (1) the cyclobutenyl group is staggered with respect to the equatorial $(CO)_2$(bipy) plane. The metal-carbon distances vary considerably with Mo-C(4) (*i.e.* to the carbonyl) the longest at 2.563(10) Å. The Mo-C(2), C(3) distances are virtually identical at 2.328(10), 2.340(10) Å and Mo-C(1) is the shortest at 2.234(10) Å. A similar set of distances was found in $[Co(CO)_3(C_4Ph_3O)]$ [14] (*viz.* 2.405; 2.104, 2.117; 1.999 Å: mean values are quoted from the two molecules in the asymmetric unit). Allowing for the difference in radii, the M–C distances follow a similar trend despite the difference in geometry and configuration for the two molecules. This suggests that the variation in bond length M–C(*n*) is an electronic rather than a steric effect.

However, steric factors are important in the overall geometry of the C_4Ph_3O ligand. Thus the most strongly bound carbon atom [C(1)] occupies the least crowded

TABLE 4

Molecular dimensions,* distances (Å) and angles (°), for (1) and (2)

	(1)	(2)
(*a*) Metal co-ordination spheres		
Mo–Br	2.619(1)	2.626(3)
Mo–C(7)	1.990(11)	1.992(24)
Mo–C(8)	2.005(12)	1.990(25)
Mo–N(52)	2.211(8)	2.223(19)
Mo–N(62)	2.233(8)	2.221(17)
Mo–C(1)	2.234(10)	2.193(18)
Mo–C(2)	2.328(10)	2.204(26)
Mo–C(3)	2.340(10)	2.262(22)
Mo–C(4)	2.563(10)	
Br–Mo–C(7)	82.22(30)	86.6(8)
Br–Mo–C(8)	77.99(32)	84.8(8)
Br–Mo–N(52)	81.16(22)	84.3(5)
Br–Mo–N(62)	81.54(21)	83.0(5)
Br–Mo–C(1)	154.06(27)	159.4(6)
Br–Mo–C(2)	152.13(24)	157.7(5)
Br–Mo–C(3)	154.99(27)	156.9(4)
Br–Mo–C(4)	154.85(24)	
C(7)–Mo–N(62)	162.52(38)	167.0(10)
C(8)–Mo–N(62)	95.06(40)	96.5(8)
N(52)–Mo–N(62)	73.96(34)	75.5(7)
C(1)–Mo–N(62)	119.84(35)	80.7(7)
C(2)–Mo–N(62)	82.41(33)	94.4(7)
C(3)–Mo–N(62)	109.03(33)	118.6(5)
C(4)–Mo–N(62)	76.23(31)	
C(7)–Mo–N(52)	97.15(41)	95.7(8)
C(8)–Mo–N(52)	157.69(38)	167.2(10)
C(1)–Mo–N(52)	117.17(34)	79.4(7)
C(2)–Mo–N(52)	115.81(34)	116.6(6)
C(3)–Mo–N(52)	80.29(34)	93.0(7)
C(4)–Mo–N(52)	81.51(33)	
C(7)–Mo–C(8)	87.86(46)	90.4(9)
C(1)–Mo–C(8)	85.13(42)	109.5(9)
C(2)–Mo–C(8)	80.91(41)	73.4(9)
C(3)–Mo–C(8)	121.96(41)	99.7(10)
C(4)–Mo–C(8)	115.29(40)	
C(1)–Mo–C(7)	77.55(40)	107.4(9)
C(2)–Mo–C(7)	115.08(39)	98.1(10)
C(3)–Mo–C(7)	83.61(39)	70.8(8)
C(4)–Mo–C(7)	118.00(38)	
(*b*) Dimensions in the allyl groups		
C(11)–C(1)	1.483(14)	1.456(20)
C(21)–C(2)	1.458(15)	1.495(21)
C(31)–C(3)	1.484(15)	1.436(23)
C(1)–C(2)	1.490(14)	1.413(30)
C(1)–C(3)	1.454(15)	1.454(26)
C(2)–C(4)	1.474(15)	
C(3)–C(4)	1.487(15)	
C(2)–C(3)		1.455(26)
C(4)–O(4)	1.241(13)	
C(12)–C(11)–C(1)	117.8(9)	121.1(13)
C(16)–C(11)–C(1)	125.2(9)	118.8(12)
C(22)–C(21)–C(2)	118.9(9)	121.0(14)
C(26)–C(21)–C(2)	124.2(10)	118.8(16)
C(32)–C(31)–C(3)	121.7(10)	120.9(13)
C(36)–C(31)–C(3)	118.0(10)	118.8(13)
C(11)–C(1)–C(2)	131.9(9)	142.1(18)
C(11)–C(1)–C(3)	130.3(7)	144.3(17)
C(2)–C(1)–C(3)	89.6(8)	61.0(14)
C(21)–C(2)–C(1)	132.6(9)	139.4(16)
C(21)–C(2)–C(4)	131.8(9)	
C(21)–C(2)–C(3)		134.1(21)
C(1)–C(2)–C(4)	89.6(8)	
C(1)–C(2)–C(3)		60.9(14)
C(2)–C(4)–C(3)	89.3(8)	
Mo–C(4)–O(4)	128.6(7)	
C(2)–C(4)–O(4)	135.4(10)	
C(3)–C(4)–O(4)	135.3(10)	
C(31)–C(3)–C(1)	134.5(9)	143.0(15)
C(31)–C(3)–C(4)	131.2(9)	
C(31)–C(3)–C(2)		142.9(22)
C(1)–C(3)–C(4)	90.9(8)	
C(1)–C(3)–C(2)		58.1(13)

TABLE 4 (*continued*)

	(1)	(2)
(*c*) Carbonyl dimensions		
C(7)–O(7)	1.158(14)	1.139(26)
C(8)–O(8)	1.134(14)	1.139(30)
Mo–C(7)–O(7)	176.9(9)	170.2(21)
Mo–C(8)–O(8)	174.5(9)	179.3(17)
(*d*) Solvent dimensions		
In (1)		
O(100)–C(101)	1.406(25)	
O(100)–C(102)	1.371(29)	
C(101)–C(104)	1.378(33)	
C(102)–C(103)	1.450(33)	
C(103)–C(104)	1.416(31)	
C(101)–O(100)–C(102)	104.5(16)	
O(100)–C(101)–C(104)	108.6(17)	
O(100)–C(102)–C(103)	112.7(17)	
C(102)–C(103)–C(104)	99.8(19)	
C(101)–C(104)–C(103)	111.4(19)	
In (2)		
N(100)–C(101)	1.14(10)	
C(102)–C(101)	1.24(12)	
N(100)–C(101)–C(102)	153(7)	

* Dimensions in the bipyridine and benzene rings are given in the Supplementary Publication.

available position (Figure 3) between the two carbonyl groups. The four-membered ring is approximately square (C–C–C angles within 1° of 90°) but slightly puckered with all four atoms 0.04 Å from the plane (Table 5, Plane 1). A useful concept for considering the position of the phenyl rings is to distinguish between a tilt and a twist angle.[6] If the centre of the ring is named C_0, then the tilt angle is defined as $(180 - \alpha)$ where α is the angle C_0–C(*n*)–C(*n*1) and the twist angle is the angle between the plane consisting of atoms C_0, C(*n*), C(*n*1) and the phenyl ring. Values for (1) and (2) are given in Table 6. In (1), as might be expected, there is an inverse relationship between tilt angle and Mo–C bond length. Thus the tilt angle is greatest for C(1) and least for C(4). The twist angles are dependent upon steric effects as is clear from Figure 3. Ring 1 [bonded to C(1)] has a low twist angle to lie between the carbonyls and rings 2 and 3 [bonded to C(2) and C(3)] have twist angles close to 90° and thus are approximately parallel to bipy. In $[\mathrm{Co(CO)_3(C_3Ph_3)}]$,[6] a molecule with much less steric crowding, the twist angles are much smaller (13.5, 19.2, and 2.9°). As shown in Figure 4, the cyclopropenyl ring in (2) adopts a conformation such that C(1) is staggered midway between the two bipy nitrogen atoms and C(2) and C(3) eclipse the two carbonyls. Again the arrangement has C_s symmetry. The Mo–C distances are probably not significantly different. Their mean value at 2.22 Å is shorter than the shortest Mo–C distances in (1). As might be expected from Mo–C distances the tilt angles are on average greater than are found in (1). The twist angle for C(1) is 82.7° and, as is shown in Figure 4, this keeps the phenyl ring well away from bipy. The values for the other two rings are relatively large at 49.1 and 73.6°, and again these values can be attributed to steric effects. The C–C–C angles in the cyclopropenyl ring are *ca.* 60°.

TABLE 5

Least-squares planes for (1) and (2). Distances of atoms from the planes are given in Å. Atoms not contributing to the planes are marked with an asterisk

In (1)

Plane 1: C(1) 0.04, C(2) −0.04, C(3) −0.04, C(4) 0.04, Mo* −2.09, O(4)* 0.14, C(11)* 0.70, C(21)* 0.33, C(31)* 0.22

Plane 2: C(7) 0.04, C(8) −0.04, N(52) −0.04, N(62) 0.04, Mo* 0.34

In (2)

Plane 1: C(1), C(2), C(3) 0.00; C(11)* 0.54, C(21)* 0.80, C(31)* 0.59, Mo* −2.06

Plane 2: C(7) 0.00, C(8) 0.00, N(52) 0.00, N(62) 0.00, Mo* 0.19

TABLE 6

Twist and tilt angles in (1) and (2)

	Tilt angle = (180 − α)/°	
Angle α	(1)	(2)
C_0–C(1)–C(11)	24.3	21.6
C_0–C(2)–C(21)	16.4	32.5
C_0–C(3)–C(31)	12.4	24.1
C_0–C(4)–O(4)	2.7	
	Twist angle/°	
C_0,C(1),C(11), and phenyl ring	27.8	82.7
C_0,C(2),C(21), and phenyl ring	87.9	49.1
C_0,C(3),C(31), and phenyl ring	78.2	73.6

The Br–Mo–L *cis* angles in both structures are much less than 90°. This is concomitant with the metal atom being out of the equatorial C,C,N,N plane in the direction of the carbocyclic ligands by distances of 0.34 Å in (1) and 0.15 Å in (2). The Br–Mo–L angles average to 81.7 and 84.7° in the two structures. It is interesting to compare these values with those found in the structure of $[\mathrm{Mo(NCS)(CO)_2(bipy)}(\eta^3\text{-allyl})]$.[16] This molecule has similar geometry to (1) and (2) in that the thiocyanate is *trans* to the allyl.* The metal atom is 1.96 Å from the plane of the allyl group [*cf.* 2.09 Å from the C_4 plane in (1) and 2.06 Å from the C_3 plane in (2)], but the Mo–C distances are 2.291(9), 2.197(9), and 2.351(12) Å to this allyl ligand. Unlike (1) and (2), angles between the thiocyanate and equatorial atoms are very different, being 79.3 and 81.9° to bipy and 88.6 and 89.9° to the carbonyls with an average angle of 84.9°. We suspect that the more regular arrangement in (1) and (2) may be due to the steric effects of the phenyl rings.

There are no intermolecular distances less than the sum of van der Waals radii. For the solvent in (1) there are only two distances less than 3.5 Å, namely O(100) ··· C(64), 3.39 Å $(1 + x,y,z)$ and C(104) ··· O(7), 3.49 Å $(x,\frac{1}{2} - y,\frac{1}{2} + z)$ and in (2) there are none less than 3.75 Å.

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* The orientation of the η^3-allyl and η^3-cyclobutenyl ligands with respect to the plane containing the ligated bipy and carbonyl groups is however different.

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