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Preparation and Reactivity of Mo(NCMe)(η^2-C_2Ph_2)$_2$(η^4-C_4Ph_4)

Su-Chin Chang[a] (張淑琴), Wen-Yann Yeh[a]* (葉文彥),
Gene-Hsiang Lee[b] (李錦祥) and Shie-Ming Peng[b] (彭旭明)
[a]*Department of Chemistry, National Sun Yat-Sen University, Kaohsiung 804, Taiwan, R.O.C.*
[b]*Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, R.O.C.*

Reaction of Mo(CO)(η^2-C_2Ph_2)$_2$(η^4-C_4Ph_4) and Me_3NO in acetonitrile solvent affords Mo(NCMe)(η^2-C_2Ph_2)$_2$(η^4-C_4Ph_4) **1**. Compound **1** reacts with trimethylphosphine to produce Mo(PMe_3)(η^2-C_2Ph_2)$_2$(η^4-C_4Ph_4) **2**, or reacts with diphenylacetylene to produce (η^5-C_5Ph_5)$_2$Mo **3** and Mo(η^2-O_2CPh)(η^4-C_4Ph_4H)(η^4-C_4Ph_4) **4**. The molecular structures of **1**, **2** and **4** have been determined by an X-ray diffraction study.

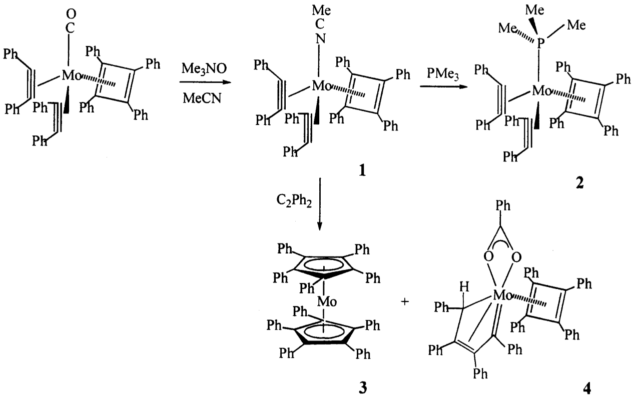
INTRODUCTION

Reactions of metal carbonyls with alkynes are known to afford a wide variety of organometallic and organic products,[1-6] such as forming the coordinative species $M_x(\text{alkyne})_y$ or through di-, tri- or tetramerization of the alkyne ligands to yield metallacyclic systems or carbocycles. Tate[7] has previously prepared the polyalkyne complex W(CO)(η^2-C_2Ph_2)$_3$ by treating W(CO)$_3$(NCMe)$_3$ with diphenylacetylene. In contrast, the analogous reaction with Mo(CO)$_3$(NCMe)$_3$ yields mainly the molybdenum tetraphenylcyclobutadiene complexes Mo(CO)(η^2-C_2Ph_2)$_2$(η^4-C_4Ph_4).[8] We have shown that W(CO)(η^2-C_2Ph_2)$_3$ is able to undergo multiple alkyne-alkyne coupling reactions under harsh conditions to form W(CO)(η^2-C_2Ph_2)$_2$(η^4-C_4Ph_4)[9] and several cyclopentadiene compounds,[10,11] including a novel tungstenocene complex (η^5-C_5Ph_5)$_2$W.[12] In the present research, we explore the reactivity of the molybdenum analogue Mo(CO)(η^2-C_2Ph_2)$_2$(η^4-C_4Ph_4).

RESULTS AND DISCUSSION

Mo(CO)(η^2-C_2Ph_2)$_2$(η^4-C_4Ph_4) is thermally robust and shows no reactions with diphenylacetylene or tertiary phosphines. It has been illustrated that replacement of the CO ligand in W(CO)(η^2-C_2Ph_2)$_3$ and W(CO)(η^2-C_2Ph_2)$_2$(η^4-C_4Ph_4) with a labile acetonitrile moiety tremendously increases their reactivity towards phosphine substitution as well as alkyne coupling reactions.[13] Thus, Mo(CO)(η^2-C_2Ph_2)$_2$(η^4-C_4Ph_4) is treated with Me_3NO in acetonitrile to afford Mo(NCMe)(η^2-C_2Ph_2)$_2$(η^4-C_4Ph_4) **1**, which reacts with PMe_3 smoothly at room temperature to produce Mo(PMe_3)(η^2-C_2Ph_2)$_2$(η^4-C_4Ph_4) **2**. Moreover, the reaction of **1** and diphenylacetylene affords the molybdenocene complex (η^5-C_5Ph_5)$_2$Mo **3** in 36% together with Mo(η^2-O_2CPh)(η^4-C_4Ph_4H)(η^4-C_4Ph_4) **4**, which contains a benzoate ligand and a Mo=C double bond (Scheme I). Compound **3** was previously obtained in low yield (ca. 4%) by heating PhC≡CPh with either Mo(CO)$_6$, Mo(CO)$_3$(NCMe)$_3$ or Mo(CO)$_3$(diglyme).[14] Thus, the present reaction provides an alternative method to prepare **3** in better yield.

Scheme I



The formation of **4** is interesting. Since the reaction in non-aromatic solvents also affords **4**, the benzoate moiety must arise from diphenylacetylene. It has been postulated that an alkylidyne moiety, M≡C-R, from alkyne C≡C bond scission is involved in certain catalytic reactions like alkyne metathesis and alkyne oligomerization.[15,16] To account for the observation herein, the reaction of **1** and diphenylacetylene is likely to generate the benzylidyne species Mo(≡CPh)(η^4-C_4Ph_4)(η^4-C_4Ph_4), which could lead to **3** *via* further C-C bond couplings or undergo hydroxidation to give **4**.

The new compounds **1**, **2** and **4** have been characterized by mass and NMR spectroscopy. In order to evaluate the electronic and steric effects of ligands on the coordination configuration around the Mo atom, their structures were determined by an X-ray diffraction study. The molecular structures of **1** and **2**, shown in Fig. 1 and Fig. 2, are closely related and resemble those observed for the tungsten analogues $W(CO)(\eta^2\text{-}C_2Ph_2)_2(\eta^4\text{-}C_4Ph_4)$[9] and $W(PMe_3)(\eta^2\text{-}C_2Tol_2)_2(\eta^4\text{-}C_4Tol_4)$.[17] If taking the centers of the alkynes and the center of cyclobutadiene, the coordination about the molybdenum atom in **1** and **2** can be described as a distorted tetrahedron.

In **1** the NCMe ligand is terminally bonded to the molybdenum atom with the angle Mo-N(1)-C(9) = 175.4(4)°. The two alkyne ligands are bonded to the molybdenum atom symmetrically, and the phenyl groups are bent back from the $C\equiv C$ vector by angles averaging 139°. The cyclobutadiene ring is about planar, which is bonded to the molybdenum atom asymmetrically with the lengths Mo-C(2) = 2.235(4) Å and Mo-C(3) = 2.268(4) Å being slightly shorter than those of Mo-C(1) = 2.337(4) Å and Mo-C(4) = 2.349(4) Å. The phenyl *ipso*-carbons C(21), C(31), C(11) and C(41) are bent away from the cyclobutadiene ring by 24, 12, 19 and 15°, respectively.

In **2** the PMe_3 group is sterically forcing the alkyne ligands and the cyclobutadiene ring from being parallel, such

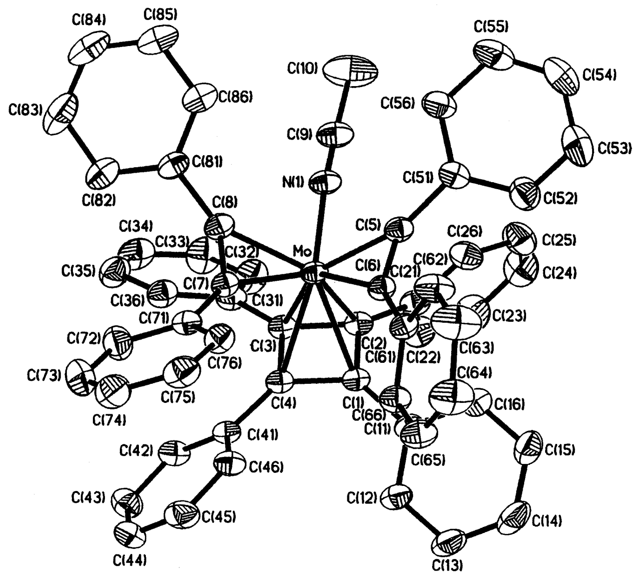


Fig. 1. Molecular structure of **1**. Selected bond distances/Å: Mo-N(1) = 2.152(3), N(1)-C(9) = 1.127(6), C(9)-C(10) = 1.465(8), Mo-C(1) = 2.337(4), Mo-C(2) = 2.235(4), Mo-C(3) = 2.268(4), Mo-C(4) = 2.349(4), Mo-C(5) = 2.082(4), Mo-C(6) = 2.088(4), Mo-C(7) = 2.099(4), Mo-C(8) = 2.092(4), C(1)-C(2) = 1.455(5), C(1)-C(4) = 1.474(6), C(2)-C(3) = 1.484(6), C(3)-C(4) = 1.454(5), C(5)-C(6) = 1.309(6), C(7)-C(8) = 1.307(6). Selected bond angles/deg: Mo-N(1)-C(9) = 175.4(4), Mo-C(1)-C(2) = 67.7(2), Mo-C(2)-C(1) = 75.3(2), Mo-C(3)-C(4) = 74.7(2), Mo-C(4)-C(3) = 68.6(2), Mo-C(5)-C(6) = 72.0(3), Mo-C(6)-C(5) = 71.5(2), Mo-C(7)-C(8) = 71.5(3), Mo-C(8)-C(7) = 72.1(3), N(1)-Mo-C(1) = 118.0(1), N(1)-Mo-C(2) = 81.3(1), N(1)-Mo-C(3) = 84.7(1), N(1)-Mo-C(4) = 121.3(1), N(1)-Mo-C(5) = 83.4(2), N(1)-Mo-C(6) = 120.0(2), N(1)-Mo-C(7) = 119.9(2), N(1)-Mo-C(8) = 83.6(2), C(2)-Mo-C(5) = 105.6(2), C(5)-Mo-C(8) = 112.1(2), C(8)-Mo-C(3) = 100.5(2), C(1)-Mo-C(6) = 86.3(2), C(6)-Mo-C(7) = 91.8(2), C(7)-Mo-C(4) = 84.6(2).

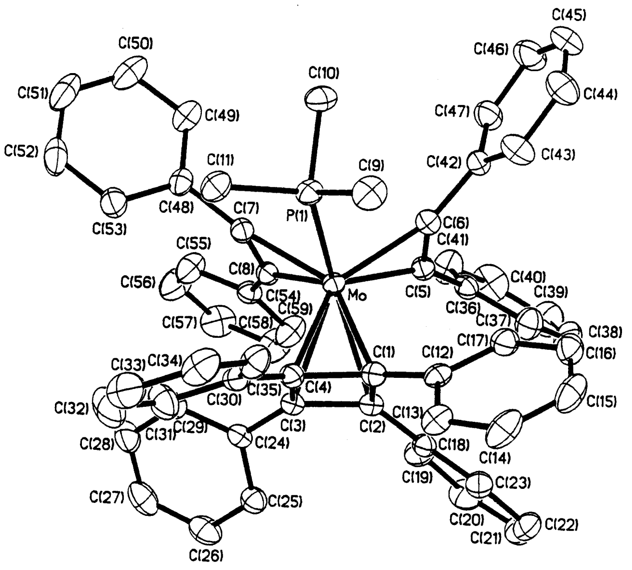


Fig. 2. Molecular structure of **2**. Selected bond distances/Å: Mo-P(1) = 2.5106(6), Mo-C(1) = 2.262(2), Mo-C(2) = 2.348(2), Mo-C(3) = 2.355(2), Mo-C(4) = 2.306(2), Mo-C(5) = 2.090(2), Mo-C(6) = 2.113(2), Mo-C(7) = 2.119(2), Mo-C(8) = 2.080(2), C(1)-C(2) = 1.459(3), C(1)-C(4) = 1.490(3), C(2)-C(3) = 1.457(3), C(3)-C(4) = 1.453(3), C(5)-C(6) = 1.301(3), C(7)-C(8) = 1.308(3). Selected bond angles/deg: Mo-C(1)-C(2) = 74.8(1), Mo-C(2)-C(1) = 68.4(1), Mo-C(3)-C(4) = 70.0(1), Mo-C(4)-C(3) = 73.7(1), Mo-C(5)-C(6) = 72.9(1), Mo-C(6)-C(5) = 71.0(1), Mo-C(7)-C(8) = 70.3(1), Mo-C(8)-C(7) = 73.5(1), P(1)-Mo-C(1) = 94.8(5), P(1)-Mo-C(2) = 131.52(5), P(1)-Mo-C(3) = 123.14(5), P(1)-Mo-C(4) = 88.40(5), P(1)-Mo-C(5) = 117.92(6), P(1)-Mo-C(6) = 82.14(6), P(1)-Mo-C(7) = 78.76(6), P(1)-Mo-C(8) = 114.77(6), C(2)-Mo-C(5) = 84.31(7), C(5)-Mo-C(8) = 91.64(8). C(8)-Mo-C(3) = 84.75(7), C(1)-Mo-C(6) = 100.56(8), C(6)-Mo-C(7) = 112.93(8), C(7)-Mo-C(4) = 106.40(8).

that C(5)C(6) is tilted from the Mo-P(1) vector by 11.0°, C(7)C(8) by 8.4°, C(1)C(2) by 20.0° and C(3)C(4) by 14°. This gives rise to a slight difference between the upper and lower C-Mo distances, such that Mo-C(6) = 2.113(2) Å, Mo-C(5) = 2.090(2) Å, Mo-C(7) = 2.119(2) Å and Mo-C(8) = 2.080(2) Å. The cyclobutadiene group (C(1) to C(4)) is about planar and bonded to the molybdenum atom asymmetrically, with Mo-C distances ranging from 2.262(2) Å through 2.355(2) Å. The phenyl *ipso*-carbons C(12), C(18), C(24) and C(30) are bent away from the cyclobutadiene ring by 19, 25, 13 and 24°, respectively. The alkyne phenyl groups are bent back from the C≡C vector by angles averaging 134°.

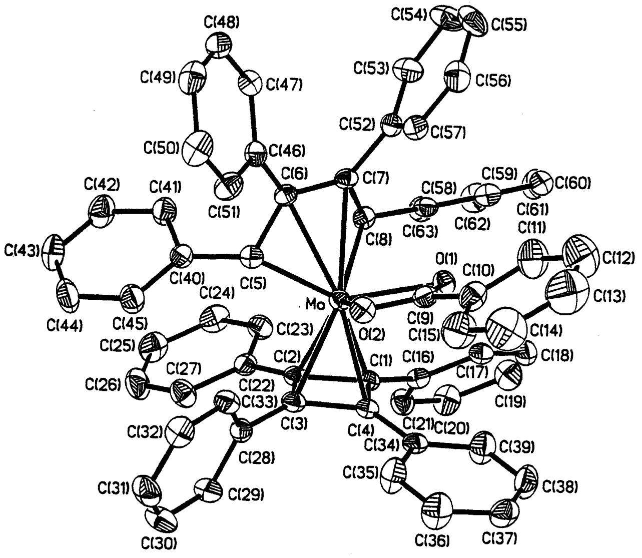


Fig. 3. Molecular structure of **4**. Selected bond distances/Å: Mo-O(2) = 2.160(2), Mo-O(1) = 2.252(2), Mo-C(9) = 2.575(3), C(9)-C(10) = 1.484(4), C(9)-O(1) = 1.264(3), C(9)-O(2) = 1.282(3), Mo-C(1) = 2.256(3), Mo-C(2) = 2.292(3), Mo-C(3) = 2.232(3), Mo-C(4) = 2.234(3), Mo-C(5) = 1.946(3), Mo-C(6) = 2.352(3), Mo-C(7) = 2.437(3), Mo-C(8) = 2.304(3), C(1)-C(2) = 1.458(4), C(1)-C(4) = 1.469(4), C(2)-C(3) = 1.460(4), C(3)-C(4) = 1.466(4), C(5)-C(6) = 1.457(4), C(6)-C(7) = 1.406(4), C(7)-C(8) = 1.447(4). Selected bond angles/deg: O(1)-Mo-O(2) = 59.18(7), O(1)-C(9)-O(2) = 117.8(2), O(1)-C(9)-C(10) = 121.1(3), O(2)-C(9)-C(10) = 121.1(3), Mo-C(5)-C(6) = 86.2(2), Mo-C(5)-C(40) = 152.2(2), C(40)-C(5)-C(6) = 121.0(2), C(5)-C(6)-C(7) = 117.2(2), C(6)-C(7)-C(8) = 118.0(2), Mo-C(8)-C(58) = 129.0(2), C(58)-C(8)-C(7) = 123.4(2). Selected torsion angles/deg: Mo-C(6)-C(5)-C(40) = 173.7(3), C(5)-C(6)-C(7)-C(8) = 9.5(3), C(40)-C(5)-C(6)-C(46) = 55.7(3), C(46)-C(6)-C(7)-C(52) = 12.1(4), C(58)-C(8)-C(7)-C(52) = 2.6(4).

The molecular structure of **4**, illustrated in Fig. 3, consists of discrete molecules with each molybdenum unit bonded to one benzoate, one tetraphenylcyclobutadiene and one tetraphenylbutadienyl ligand. The carboxylate group, cyclobutadiene ring and butadienyl group are essentially planar with the maximum atomic displacement from plane being 0.01, 0.01 and 0.03 Å, respectively. The cyclobutadiene ring is bonded to the molybdenum atom with Mo-C(3) = 2.232(3) Å and Mo-C(4) = 2.234(3) Å being slightly shorter than Mo-C(1) = 2.256(3) Å and Mo-(2) = 2.292(3) Å, and the attached phenyl *ipso*-carbons are bent away from the ring plane by angles averaging 14.0°. The benzoate group is η^2-coordinated to Mo with Mo-O(1) = 2.252(2) Å and Mo-O(2) = 2.160(2) Å. However, the weak interaction between the Mo and C(9) atoms (distance = 2.575(3) Å) could also suggest an η^3-bonding mode for the benzoate ligand. The butadienyl group (C(5)~C(8)) appears to have a molybdenum-carbon double bond to C(5) (1.946(3) Å), a single bond to C(8) (2.304(3) Å), and a π-donation from C(6) and C(7) to Mo (2.352(3) and 2.437(3) Å). Moreover, the atoms Mo, C(5), C(6) and C(40) are about on the same plane with the dihedral angle Mo-C(6)-C(5)-C(40) = 173.7(3)° and the angle C(6)-C(5)-C(40) = 121.0(2)°, implying a carbene carbon for the C(5) atom.

The results presented here describe activation of Mo(CO)(η^2-C_2Ph_2)$_2$(η^4-C_4Ph_4) by replacing the CO ligand with NCMe, which substantially increases the reactivity of the complex. The reaction patterns of **1** with PMe_3 and diphenylacetylene show great resemblance to those occurring at a tungsten center. However, more complicated results are obtained when treating **1** with bulky phosphines, such as triphenylphosphine and bis(diphenylphosphino)ferrocene, in comparison with the tungsten system.[17] The difference may be attributed to the intrinsically lower stability of the second-raw transition metal complexes than the third-raw metals.[18]

EXPERIMENTAL SECTION

General Methods

All the experimental manipulations were carried out under a dinitrogen atmosphere using standard Schlenk techniques.[19] Solvents were dried over appropriate reagents under dinitrogen.[20] Anhydrous Me_3NO was obtained from $Me_3NO \cdot 2H_2O$ (Aldrich) by sublimation under vacuum twice. $Mo(CO)_6$, PMe_3 (1.0 M in toluene) and PhC≡CPh were purchased from Aldrich and used as received. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Kieselgel DGF_{254}). $Mo(CO)(\eta^2\text{-}C_2Ph_2)_2(\eta^4\text{-}C_4Ph_4)$ was prepared as described in the literature.[21] IR spectra were taken on a Hitachi I-2001 spectrometer. MS spectra were obtained on a VG Blotch-5023 mass spectrometer. NMR spectra were recorded on a Varian VXR-300 spectrometer. Elemental analysis was performed at the National Chen-Kung University, Tainan.

Preparation of $Mo(NCMe)(\eta^2\text{-}C_2Ph_2)_2(\eta^4\text{-}C_4Ph_4)$

$Mo(CO)(\eta^2\text{-}C_2Ph_2)_2(\eta^4\text{-}C_4Ph_4)$ (670 mg, 0.80 mmol) and dichloromethane (10 mL) were introduced into an oven-dried 100 mL Schlenk flask, equipped with a magnetic stir bar and a rubber serum stopper, under dinitrogen atmosphere. A solution of Me_3NO (185 mg) in acetonitrile (5 mL) was introduced into the flask via a syringe through the serum stopper. The mixture was stirred at room temperature for 2 h and then in an oil bath (50 °C) for another 2 h, at which point the IR spectrum showed no ν_{CO} absorption due to the starting compound. The mixture was passed through a short silica gel column to remove the remaining Me_3NO, and the solvents were removed on a rotary evaporator. The residue was crystallized twice from dichloromethane/*n*-hexane to afford dark purple crystals of $Mo(NCMe)(\eta^2\text{-}C_2Ph_2)_2(\eta^4\text{-}C_4Ph_4)$ **1** (420 mg, 0.50 mmole, 62%). MS FAB *m/z*: 849 (M^+, ^{96}Mo), 808 (M^+-NCMe). ^1H NMR (CD_2Cl_2, 20 °C): 7.37-6.84 (m, Ph), 1.97 (s, NCMe) ppm. Anal. For $C_{58}H_{43}NMo$: Found C, 81.94; H, 5.03; N, 1.63; Calc. C, 81.96; H, 5.10; N, 1.65.

Preparation of $Mo(PMe_3)(\eta^2\text{-}C_2Ph_2)_2(\eta^4\text{-}C_4Ph_4)$

Compound **1** (150 mg, 0.18 mmol) and dichloromethane (10 mL) were placed in a 50 mL Schlenk flask under dinitrogen. PMe_3 (0.3 mmol) was added into the flask and the resulting mixture was stirred at room temperature for 12 h. The volatile materials were removed under vacuum, and the residue was subjected to TLC with dichloromethane/*n*-hexane (3:1, v/v) as eluant. Crystallization of the material forming the major purple-red band from dichloromethane/*n*-hexane produced dark red crystals of $Mo(PMe_3)(\eta^2\text{-}C_2Ph_2)_2(\eta^4\text{-}C_4Ph_4)$ (**2**, 34 mg, 22%). MS FAB *m/z*: 884 (M^+, ^{96}Mo), 808 (M^+-PMe_3). ^1H NMR (CD_2Cl_2, 20 °C): 7.24-6.78 (m, Ph), 0.93 (d, $^2J_{P\text{-}H}$ = 5 Hz, Me) ppm. $^{31}P\ \{^1H\}$ NMR (CD_2Cl_2, 20 °C): -17.02 (s) ppm.

Reaction of 1 with Diphenylacetylene

A solution of compound **1** (100 mg, 0.12 mmol) and diphenylacetylene (107 mg, 0.6 mmol) in toluene (5 mL) was heated to reflux under dinitrogen for 10 min. The mixture was cooled to ambient temperature and filtered. The red solid precipitate was washed with dichloromethane, dried under vacuum, and characterized as the known $(\eta^5\text{-}C_5Ph_5)_2Mo$ (**3**, 40

Table 1. Crystal Data and Refinement Details for Compounds **1**, **2** and **4**

	1	**2**	**4**
Formula	$C_{58}H_{43}MoN$	$C_{59}H_{49}MoP$	$C_{63}H_{46}MoO_2$
T (K)	295(2)	295(2)	150(2)
Crystal system	triclinic	orthorhombic	triclinic
Crystal solvent	CH_2Cl_2		CH_2Cl_2
Space group	P $\bar{1}$	Pbca	P $\bar{1}$
Unit cell dimensions			
a/Å	12.3453(2)	18.3613(6)	12.4535(4)
b/Å	12.8798(2)	18.6957(6)	13.4417(4)
c/Å	16.4718(2)	26.2646(9)	16.4928(5)
α/deg	76.666(1)	90	84.650(1)
β/deg	84.320(1)	90	69.791(1)
γ/deg	75.175(1)	90	73.091(1)
V/Å^3	2461.43(6)	9016.0(5)	2478.78(13)
Z	2	8	2
D_{calcd}/g cm^{-3}	1.261	1.304	1.361
F(000)	964	3680	1048
Radiation (λ/Å)	0.71073	0.71073	0.71073
μ/mm^{-1}	0.413	0.365	0.419
θ range/deg	2.31-27.45	1.55-27.50	1.32-27.50
R_1	0.0653	0.0312	0.0402
wR_2	0.1868	0.0684	0.0798
Goodness-of-fit on F^2	1.086	1.033	1.027

Table 2. Selected Atomic Coordinates (× 10^4) of Compound **1**

Atom	x	y	z	U_{eq}
Mo	6916(1)	5148(1)	7368(1)	44(1)
N(1)	5826(3)	5681(3)	6333(2)	57(1)
C(1)	8512(3)	5841(3)	7253(2)	49(1)
C(2)	7931(3)	6153(4)	6474(2)	50(1)
C(3)	8318(3)	4999(3)	6371(2)	49(1)
C(4)	8875(3)	4691(3)	7159(2)	48(1)
C(5)	5683(4)	6270(4)	7890(3)	53(1)
C(6)	6466(3)	5811(3)	8431(2)	48(1)
C(7)	7149(3)	3537(3)	8081(2)	49(1)
C(8)	6479(4)	3654(4)	7483(3)	55(1)
C(9)	5224(4)	6021(5)	5811(3)	69(1)
C(10)	4385(7)	6481(9)	5171(4)	129(3)
C(11)	8873(4)	6496(4)	7736(3)	53(1)
C(21)	7608(4)	7242(4)	5898(3)	55(1)
C(31)	8329(3)	4444(4)	5681(2)	53(1)
C(41)	9730(3)	3740(3)	7565(2)	48(1)
C(51)	4660(4)	7164(4)	7758(3)	56(1)
C(61)	6639(4)	5849(4)	9288(2)	51(1)
C(71)	7598(4)	2708(4)	8811(3)	54(1)
C(81)	5798(4)	3047(4)	7189(3)	59(1)

Table 3. Selected Atomic Coordinates (× 10^4) of Compound **2**

Atom	x	y	z	U_{eq}
Mo	6819(1)	2536(1)	6169(1)	29(1)
P(1)	7581(1)	2428(1)	5380(1)	38(1)
C(1)	7152(1)	3676(1)	6336(1)	34(1)
C(2)	6599(1)	3506(1)	6716(1)	33(1)
C(3)	6036(1)	3509(1)	6326(1)	34(1)
C(4)	6570(1)	3702(1)	5942(1)	35(1)
C(5)	7186(1)	2025(1)	6829(1)	35(1)
C(6)	7703(1)	1973(1)	6492(1)	36(1)
C(7)	6147(1)	1881(1)	5708(1)	36(1)
C(8)	5868(1)	1931(1)	6164(1)	34(1)
C(9)	8439(1)	2926(1)	5343(1)	56(1)
C(10)	7883(1)	1513(1)	5266(1)	51(1)
C(11)	7179(1)	2634(1)	4761(1)	51(1)
C(12)	7887(1)	3980(1)	6421(1)	35(1)
C(18)	6590(1)	3607(1)	7274(1)	35(1)
C(24)	5229(1)	3504(1)	6353(1)	37(1)
C(30)	6520(1)	4063(1)	5445(1)	40(1)
C(36)	7097(1)	1808(1)	7365(1)	37(1)
C(42)	8400(1)	1589(1)	6488(1)	39(1)
C(48)	5918(1)	1509(1)	5241(1)	40(1)
C(52)	5248(1)	1462(2)	4455(1)	75(1)

Table 4. Selected Atomic Coordinates (× 10^4) of Compound **4**

Atom	x	y	z	U_{eq}
Mo	12034(1)	3326(1)	1969(1)	18(1)
O(1)	12296(2)	1693(1)	1567(1)	24(1)
O(2)	11470(2)	3044(2)	932(1)	25(1)
C(1)	13969(2)	3134(2)	1768(2)	21(1)
C(2)	13340(2)	4228(2)	1966(2)	20(1)
C(3)	13104(2)	4352(2)	1149(2)	21(1)
C(4)	13774(2)	3263(2)	932(2)	19(1)
C(5)	10813(2)	4509(2)	2623(2)	20(1)
C(6)	10071(2)	3800(2)	2943(2)	20(1)
C(7)	10587(2)	2829(2)	3245(2)	19(1)
C(8)	11735(2)	2666(2)	3344(2)	20(1)
C(9)	11844(3)	2053(2)	986(2)	24(1)
C(10)	11726(3)	1352(2)	397(2)	32(1)
C(16)	14785(2)	2339(2)	2128(2)	21(1)
C(22)	13226(2)	4939(2)	2638(2)	22(1)
C(28)	12695(3)	5239(2)	611(2)	22(1)
C(34)	14233(2)	2661(2)	120(2)	22(1)
C(40)	10408(2)	5578(2)	2968(2)	23(1)
C(46)	8836(3)	4130(2)	2906(2)	22(1)
C(52)	9984(2)	1977(2)	3390(2)	23(1)
C(58)	12394(2)	1664(2)	3632(2)	21(1)

mg, 36%). The filtrate was evaporated to dryness on a rotary evaporator. The residue was subjected to TLC with dichloromethane/*n*-hexane (3:7, v/v) as eluant. The first band recovered the unreacted diphenylacetylene. The second band was the unreacted **1**. Crystallization of the material forming the third red band from dichloromethane/*n*-hexane afforded dark red crystals of Mo(η^2-O_2CPh)(η^4-C_4Ph_4H)(η^4-C_4Ph_4) (**4**, 3 mg, 3%). MS FAB *m/z*: 930 (M^+, ^{96}Mo). ^{1}H NMR (CD_2Cl_2, 20 °C): 7.80-7.05 (m, Ph, CHPh) ppm.

Structure Determination for 1, 2 and 4

A crystal of **1** (ca. $0.20 \times 0.13 \times 0.05$ mm^3), a crystal of **2** (ca. $0.27 \times 0.25 \times 0.12$ mm^3) and a crystal of **4** (ca. $0.18 \times 0.16 \times 0.05$ mm^3) were each mounted in a thin-walled glass capillary and aligned on the Nonius Kappa-CCD (for **1**), Brucker SMART-CCD (for **2**) and Simens SMART-CCD (for **4**) diffractometers, respectively, with graphite-monochromated Mo-K_α radiation. The data were collected at 295(2) K for **1** and **2** and 150(2) K for **4**. All data were corrected for the effects of absorption. The structures were solved by the direct method and refined by full-matrix least square on F^2. The program used was the SHELXTLE package.[22] All non-hydrogen atoms were refined with anisotropic displacement parameter. Hydrogen atoms were included but not refined. The data collection and refinement parameters are presented in Table 1. Selected atomic positional parameters for **1**, **2** and **4** are given in Table 2, 3 and 4, respectively.

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Key Words

Molybdenum; Molybdenocene; Alkyne coupling; Cyclobutadiene complexes.

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