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Studies on olefin-coordinating transition metal-carbene complexes

VII *. Studies on the synthesis, spectra and structure of cycloheptatriene(dicarbonyl)[ethoxy(aryl)carbene]-molybdenum and -chromium, and bicycloheptadiene(tricarbonyl)-[ethoxy(aryl)carbene]molybdenum complexes

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Abstract

Reaction of cycloheptatriene(tricarbonyl)-molybdenum (I) and -chromium (II), and bicycloheptadiene(tetracarbonyl)molybdenum (III) with aryllithium, ArLi (Ar = C_6H_5, *p*-, *o*-, *m*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-CF_3-C_6H_4), in ether at low temperature, and subsequent alkylation of the acylmetallate formed with Et_3OBF_4 in aqueous solution at 0 °C, gave 10 crystalline complexes with the compositions $C_7H_8(CO)_2MoC(OC_2H_5)Ar$ (IV–VII), $C_7H_8(CO)_2CrC(OC_2H_5)C_6H_4CF_3$-*p* (VIII) and $C_7H_8(CO)_3MoC(OC_2H_5)Ar$ (IX–XIII) formulated as cycloheptatriene(dicarbonyl)[ethoxy(aryl)carbene]-molybdenum and -chromium, and bicycloheptadiene (tricarbonyl)[ethoxy(aryl)carbene]molybdenum complexes, respectively. When C_6H_5Li or *p*-, *o*-$CH_3C_6H_4Li$ was allowed to react with II under the same conditions, deprotonation at the saturated carbon atom of the cycloheptatriene ligand occurred. After treatment with CH_3I, the 7-*exo*-(methylcycloheptatriene)tricarbonylchromium was obtained. The products IV–XIII were identified by elemental analyses, IR, ^1H NMR and mass spectra, and finally confirmed by the single crystal X-ray structure determinations of VI and XII.

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* Part VI see Acta Chimica Sinica, in press.

Introduction

We have recently reported that the reaction of butadiene- and isoprene(tricarbonyl)iron with aryllithium nucleophiles at low temperature generates acylmetallate intermediates which react with Et_3OBF_4 to yield a group of novel isomerized butadiene- and isoprene (dicarbonyl)[ethoxy(aryl)carbene]iron complexes [1,2], respectively. More recently we discovered that the reactions between cyclooctatetraene(tricarbonyl)iron and aryllithium afford a series of novel isomerized products of cyclooctatetraene(dicarbonyl)[ethoxy(aryl)carbene]iron and/or 8-dihydro-3,4,5-η-cyclooctatrienyl(tricarbonyl)aryliron complexes [3]. The structures of these products showed a variety of bonding modes for the olefins in the organometallic compounds. We now report analogous chemistry for cycloheptatriene(tricarbonyl)-molybdenum (I) and -chromium (II), and bicycloheptadiene(tetracarbonyl)molybdenum (III), in which the olefin ligands are a conjugated cyclotriene and a unconjugated bicyclodiene, in order to study the effect of various olefin ligands and different central metals on the reaction products.

The cycloheptatriene (dicarbonyl)[ethoxy(aryl)carbene]-molybdenum and -chromium, and bicycloheptadiene(tricarbonyl)[ethoxy(aryl)carbene]molybdenum complexes were obtained by the reaction of compounds I, II and III with aryllithium in a similar manner as previously described [1–3]. Herein we report the synthesis, spectral studies and single crystal X-ray structure determinations of these new complexes.

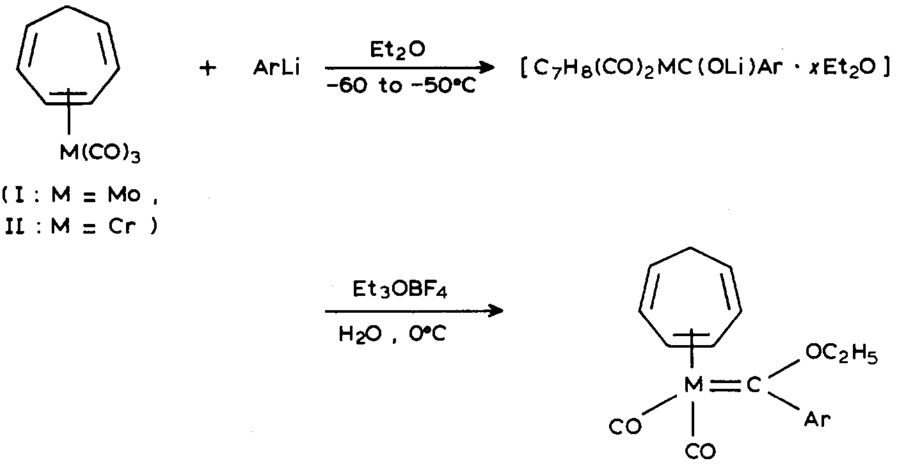
Results and discussion

Preparation of complexes (Scheme 1)

Equimolar quantities of the molybdenum complex I and aryllithium, ArLi ($Ar=C_6H_5$, p-,o-$CH_3C_6H_4$, p-$CF_3C_6H_4$), were allowed to react in ether at low temperature. The acylmetallates thus formed were subsequently alkylated with Et_3OBF_4 in aqueous solution at 0 ° C. The resulting products were chromatographed on an alumina column at low temperature and recrystallized from pentane solution at −80 ° C to give red crystalline complexes IV–VII with the general composition $C_7H_8(CO)_2MoC(OC_2H_5)Ar$.

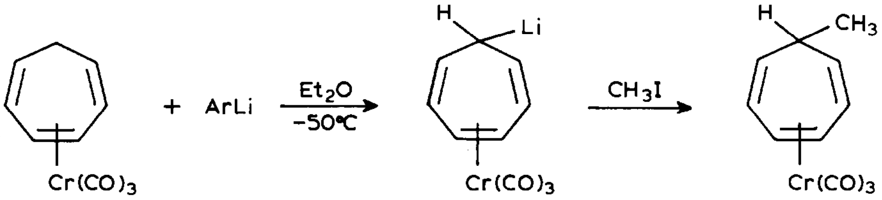
Interestingly, the chromium complex II reacted with aryllithium under the same conditions only in the case of p-$CF_3C_6H_4Li$. The acylmetallate compound formed was alkylated with Et_3OBF_4 to give the analogous crystalline compound $C_7H_8(CO)_2CrC(OC_2H_5)C_6H_4CF_3$-$p$ (VIII). However, C_6H_5Li or p-,o-$CH_3C_6H_4Li$ gave no analogous acylmetallate compounds, but only 7-*exo*-(lithiumcycloheptatriene)tricarbonylchromium, as an orange precipitate, produced by deprotonation at the saturated carbon atom of the cycloheptatriene ring. After treatment with iodomethane, the 7-*exo*-(methylcycloheptatriene)tricarbonylchromium, 7-*exo*-$(CH_3C_7H_7)Cr(CO)_3$ [4,5], was obtained. This may be due to the basicity of the aryllithium reagents. The less basic p-$CF_3C_6H_4Li$ only attacked the CO ligand of II during the reaction to yield an acylmetallate compound which was subsequently alkylated with Et_3OBF_4 to produce the carbene chromium complex VIII.

The reaction of the molybdenum diene complex III with ArLi ($Ar = C_6H_5$, p-,o-,m-$CH_3C_6H_4$, p-$CH_3OC_6H_4$) and subsequent alkylation with Et_3OBF_4 under the same conditions gave the orange-red crystalline complexes IX–XIII having the



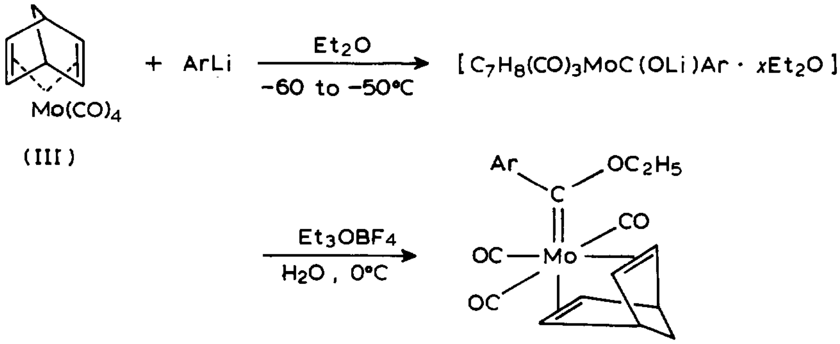
(I : M = Mo ,
II : M = Cr)

(IV : M = Mo , Ar = C_6H_5 ;
V : M = Mo , Ar = p-$CH_3C_6H_4$;
VI : M = Mo , Ar = o-$CH_3C_6H_4$;
VII : M = Mo , Ar = p-$CF_3C_6H_4$;
VIII : M = Cr , Ar = p-$CF_3C_6H_4$)



(II)

(Ar = C_6H_5 or p-, o-$CH_3C_6H_4$)



(III)

(IX : Ar = C_6H_5 ;
X : Ar = m-$CH_3C_6H_4$;
XI : Ar = o-$CH_3C_6H_4$;
XII : Ar = p-$CH_3C_6H_4$;
XIII : Ar = p-$CH_3OC_6H_4$)

general composition $C_7H_8(CO)_3MoC(OC_2H_5)Ar$. Unexpectedly, when p-$CF_3C_6H_4Li$ was used for the reaction with III, no similar product was obtained.

The complexes IV–XIII were all soluble both in polar and non-polar organic solvents. The molybdenum complexes IV–VII were rather sensitive to air and temperature. Under N_2 atmosphere they were stable for short periods in the crystalline state at room temperature. The chromium complex VIII was extremely sensitive to air and temperature in solid state, as well as in solution. On the basis of elemental analyses, IR, ^1H NMR and mass spectral analyses, and final corroboration by single crystal X-ray diffractions of VI and XII, the complexes IV–VIII and IX–XIII are formulated as cycloheptatriene(dicarbonyl)[ethoxy(aryl)carbene]-molybdenum and -chromium, and bicycloheptadiene(tricarbonyl)[ethoxy-(aryl)carbene]molybdenum complexes, respectively. These complexes are new examples of metal carbene complexes with a coordinated alkene which is not chelated to the carbene ligand. Only a few analogous non-chelated metal-carbene-alkene complexes have hitherto been reported by Rosenblum [6] and Schrock et al. [7].

Spectra studies

Infrared spectra. The metal carbonyl compounds IV–VIII of the $(CO)_2MLL'$ type gave the two expected CO absorption peaks with identical intensity. The complexes IX–XIII have pseudo octahedral geometry with a meridional arrangement of three CO ligands. These meridional complexes should possess three IR stretching bands $(2A_1 + B_1)$. Consistent with this assignment, the complexes IX–XIII showed three strong CO absorption bands in the $\nu(CO)$ region as shown in Table 1. The detailed studies on infrared spectra will be described in another report [8].

^1H NMR spectra. The ^1H NMR spectra of complexes IV–XIII in acetone-d_6 at 20 °C are given in Table 2. For each of the complexes IV–XIII, except VI, VIII and XI, two sets of resonances for the ethoxy group were seen at δ 5.52–5.64 and 5.36–5.40 ppm for OCH_2 and at δ 1.62–1.64 and 1.10–1.12 ppm for OCH_2CH_3 for IV, V and VII, and at δ 3.68–3.78 and 3.52–3.58 ppm for OCH_2 as well as at δ 1.22–1.32 and 1.10–1.12 ppm for OCH_2CH_3 for IX, X, XII and XIII. This suggested that in solution there existed, as in $(CO)_5CrC(OCH_3)C_6H_5$ [9], two *cis–trans* geometrical isomers arising from the difference in steric arrangement of

Table 1

IR spectra of the complexes IV–XIII

Complex	$\nu(CO)$ (cm^{-1})	
	CH_2Cl_2	Hexane
IV	1926vs, 1855vs	1940vs, 1878vs
V	1923vs, 1854vs	1939vs, 1880vs
VI	1935vs, 1867vs	1952vs, 1892vs
VII	1932vs, 1864vs	1949vs, 1888vs
VIII	1927vs, 1877vs	1940vs, 1898vs
IX		2020m, 1945vs, 1929vs
X		2020m, 1946vs, 1933vs
XI		2019m, 1945vs, 1931vs
XII		2018m, 1945vs, 1930vs
XIII		2016m, 1936vs, 1925vs

Table 2

^{1}H NMR spectra of complexes IV–XIII in acetone-d_6 at 20 °C (δ(ppm), TMS as internal reference)

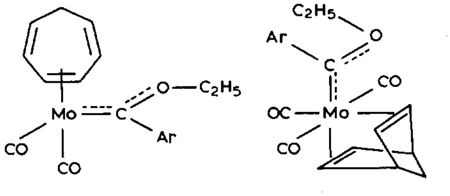
Complex	δ(cycloolefin-proton)	$\delta(\mathrm{O}CH_2\mathrm{CH_3})$		Molecular ratio *trans/cis*	$\delta(\mathrm{OCH_2}CH_3)$		Molecular ratio *trans/cis*	δ(aryl-proton)
		trans	*cis*		*trans*	*cis*		
IV	6.59(t,2), 6.16(m,1), 5.58(m,1) 3.59(q,2), 2.23(t,2)	5.38	4.96	0.55	1.65	1.12	1.05	7.75(m,2), 7.34(m,3)
V	6.60(t,2), 6.15(m,1), 5.54(m,1) 3.58(q.2), 2.26(t,2)	5.36	4.94	0.58	1.62	1.10	1.40	7.70(m,2), 7.20(m,2) 2.34(s,3)(p-$CH_3\mathrm{C_6H_4}$)
VI	6.60(t,2), 6.18(m,2), 3.57(q,2) 2.22(t,2)	5.37			1.12			7.45(m,2), 7.15(m,2) 2.59(o-$CH_3\mathrm{C_6H_4}$)
VII	6.59(t,2), 6.16(m,1), 5.64(m,1) 3.57(q,2), 2.22(t,2)	5.40	4.98	0.60	1.64	1.12	0.68	7.82(m,2), 7.70(m,2)
VIII	6.12(t,2), 5.22(m,2), 3.56(q,2) 2.38(t,2)	4.16			1.00			7.90(m,2), 7.72(m,2)
IX	5.24(t,4), 3.86(m,2), 1.35(t,2)	3.76	3.58	0.42	1.30	1.12	1.50	7.48(m,2), 7.34(m,3)
X	5.24(t,4), 3.85(m,2), 1.36(t,2)	3.72	3.52	0.90	1.32	1.12	1.05	7.42–7.0(m,4) 2.34(s, 3)(m-$CH_3\mathrm{C_6H_4}$)
XI	5.22(t,4), 3.84(m,2), 1.35(t,2)	3.56			1.14			7.50–7.08(m,4) 2.32(s,3)(o-$CH_3\mathrm{C_6H_4}$)
XII	5.25(t,4), 3.85(m,2), 1.35(t,2)	3.68	3.54	1.40	1.22	1.10	1.60	7.36(m,2), 7.20(m,2) 2.32(s,3)(p-$CH_3\mathrm{C_6H_4}$)
XIII	5.18(t,4), 3.88(m,2), 1.35(t,2)	3.78	3.58	1.75	1.28	1.12	0.70	7.33(m,2), 6.86(m,2) 3.81(s,3)(p-$CH_3\mathrm{OC_6H_4}$)

Table 3

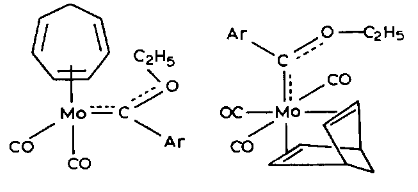
Mass spectra of the complexes IV–VIII ($M = C_7H_8(CO)_2mC(OC_2H_5)Ar$ (m = Mo, Cr), relative intensity in parentheses)

ion	IV	V	VI	VII	VIII
M^+	380(16.52)	394(2.74)	394(4.50)	448(2.70)	
$M-CO^+$	352(28.83)	366(19.32)	366(46.38)	420(44.95)	374(2.3)
$M-2CO^+$	324(9.81)	338(5.48)	338(13.99)	392(33.92)	346(3.5)
$M-2CO-C_2H_5{}^+$	295(100.0)	309(51.33)	309(74.73)	363(49.80)	317(1.99)
$M-2CO-OC_2H_5{}^+$	279(87.02)	293(14.52)	293(32.84)	347(13.89)	301(0.81)
$M-2CO-C_2H_5OH^+$	278(60.08)	292(25.92)	292(49.37)	346(13.71)	
$M-2CO-COC_2H_5{}^+$	267(19.57)	281(8.84)	281(17.84)	335(3.99)	289(0.42)
$mCOAr^+$	203(12.96)	217(6.72)	217(4.40)	271(3.72)	
$mCC_7H_8{}^+$	202(18.46)	202(9.58)	202(68.30)	202(27.46)	156(0.71)
$mC_7H_8{}^+$	190(60.60)	190(12.29)	190(14.90)	190(8.25)	144(0.29)
$mCAr^+$	187(47.09)	201(8.40)	201(43.75)	255(2.60)	209(0.36)
mAr^+	175(10.65)	189(25.07)	189(48.91)	243(5.19)	
$COC_2H_5Ar^+$	134(11.99)	148(2.40)	148(3.30)	202(27.46)	202(2.45)
$ArCO^+$	105(12.08)	119(45.49)	119(19.57)	173(29.63)	173(0.73)
m^+	98(20.17)	98(5.87)	98(12.88)	98(2.50)	52(1.24)
$C_7H_8{}^+$	92(23.09)	92(36.32)	92(36.01)	92(30.84)	92(1.38)
$C_7H_8-H^+$	91(59.79)	91(100.0)	91(100.0)	91(100.0)	91(0.39)
Ar^+	77(46.17)	91(100.0)	91(100.0)	145(21.78)	145(1.21)

the ethyl and aryl groups with regard to the $C_{carbene}$–O partial double bond. However, in the case of the complexes VI and XI, as in $C_8H_8(CO)_2FeC(OC_2H_5)C_6H_4CH_3$-*o* [3], no analogous *cis–trans* isomers were obtained in solution, perhaps owing to the steric hindrance of the methyl group of the *o*-tolyl substituent or due to rapid *cis–trans* isomerization.



cis



trans

Mass spectra. The mass spectra of the complexes IV–XIII showed a series of characteristic ion peaks with structural significance. All except complex VIII showed their molecular ions and the principal fragments produced by successive loss of CO ligands. In addition, ion peaks from fragmentation generated by further cleavage of these principal fragments (Tables 3 and 4) were seen. Complex VIII showed no molecular ion peak, but showed the essential characteristic fragments of the molecule.

Molecular structure of the complexes VI and XII

Based on the results of crystal structure determinations, the molecular configuration of VI and XII are shown in Fig. 1 and 2, respectively.

Table 4

Mass spectra of the complexes IX–XIII ($M = C_7H_8(CO)_3MoC(OC_2H_5)Ar$, relative intensity in parentheses)

ion	IX	X	XI	XII	XIII
M^+	408(8.75)	422(2.52)	422(11.81)	422(1.85)	438(1.02)
	406(6.87)	420(1.65)	420(10.41)	420(1.72)	436(1.00)
$M-CO^+$	378(17.69)	392(2.40)	392(24.42)	392(1.54)	408(1.15)
$M-CO-C_2H_5{}^+$	349(5.25)	363(weak)	363(49.25)	363(1.62)	379(1.76)
$M-2CO^+$	350(5.92)	364(1.84)	364(49.55)	364(1.87)	380(weak)
$M-2CO-C_2H_5{}^+$	321(8.18)	335(1.70)	335(17.71)	335(5.60)	351(2.01)
$M-3CO^+$	322(9.68)	336(2.03)	336(20.02)	336(6.52)	352(2.25)
$M-3CO-C_2H_5{}^+$	293(3.08)	307(1.67)	307(8.10)	307(2.01)	323(2.30)
$M-3CO-OC_2H_5{}^+$	277(3.18)	291(1.58)	291(23.52)	291(1.55)	307(0.87)
$M-3CO-C_2H_5OH^+$	276(5.64)	290(1.62)	290(22.42)	290(1.70)	306(1.36)
$M-3CO-COC_2H_5{}^+$	265(4.36)	279(9.27)	279(14.01)	279(1.84)	295(2.18)
$C_7H_8COC_2H_5Ar^+$	240(4.00)	240(48.11)	240(96.69)	240(100.00)	240(2.58)
$MoCOAr^+$	201(2.57)	215(1.32)	215(4.60)	215(0.67)	
$MoCC_7H_8{}^+$	200(2.62)	200(1.68)	200(6.20)	200(1.49)	200(1.21)
$MoC_7H_8{}^+$	188(17.69)	188(11.47)	188(24.92)	188(1.66)	188(12.46)
$MoCAr^+$	185(11.86)	199(4.64)	199(8.50)	199(6.79)	215(8.45)
$MoAr^+$	173(3.73)	187(8.96)	187(18.41)	187(1.29)	203(0.80)
$COC_2H_5Ar^+$	134(3.11)	148(2.91)	148(0.38)		164(2.86)
$ArCO^+$	105(75.79)	119(55.48)	119(76.87)	119(62.33)	135(100.00)
Mo^+	96(3.33)	96(2.01)	96(6.20)	96(1.74)	96(2.67)
$C_7H_8{}^+$	92(41.09)	92(42.35)	92(28.52)	92(24.85)	92(47.59)
$C_7H_8-H^+$	91(100.00)	91(100.00)	91(100.00)	91(72.90)	92(96.89)
Ar^+	77(40.75)	91(100.00)	91(100.00)	91(72.90)	107(10.97)

The structure analyses demonstrated that the bonding mode for the central metal and ligands in both molecular structures is governed by the 18-electron rule. In molecule VI, the central Mo atom is bonded to C(1), C(2), C(3), C(4), C(6), C(7), C(8), C(9) and C(10) to satisfy the 18-electron rule, among which, each of the two

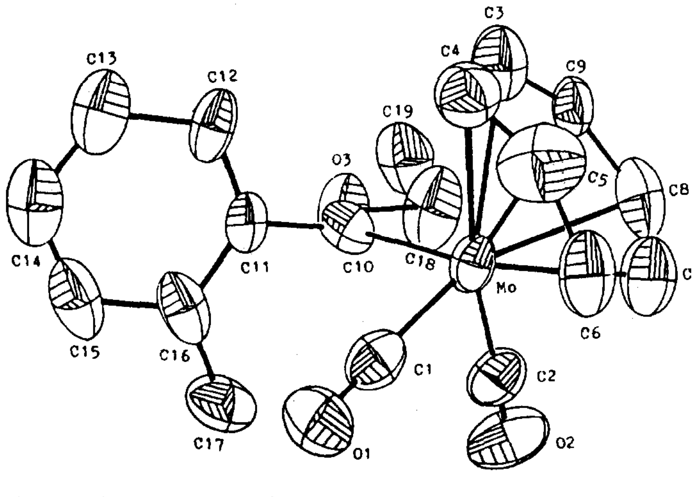


Fig. 1. Molecular structure of VI.

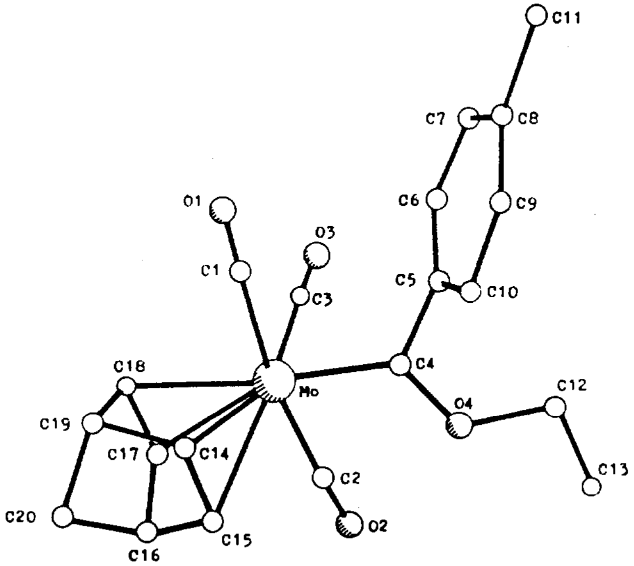


Fig. 2. Molecular structure of XII.

CO ligands contributed a pair of bonding electrons. In the cycloheptatriene ligand, from the data of bond lengths of Mo–C bond (2.31–2.50 Å) given in Table 7 it can be seen that except for the sp^3 hybridized C(5) atom, the corresponding six π-electrons of the other six carbon atoms C(3), C(4), C(6), C(7), C(8) and C(9)) evidently participate in π_6^6 non-localized π-bonding orbitals to form the d-π bond with the atomic orbitals of Mo. In addition, the carbene carbon C(10) bonding to ethoxy and o-tolyl group should provide a pair of electrons to form the bond with the Mo atom.

The sum of three bond angles around the C(10) atom (C(11)–C(10)–O(3) 104.3°, Mo–C(10)–O(3) 133.6°, Mo–C(10)–C(11) 122.1°) is exactly 360°, which indicates that the C(10) atom is coplanar strictly with three linking atoms (Mo, C(11) and O(3)) by using its sp^2 hybridized orbitals to form three σ bonds and leave its pure P_z orbital forming a π bond with Mo atom. According to the bond lengths of Mo–C(10) (2.053 Å), Mo–C(1) (1.969 Å) and Mo–C(2) (1.956 Å), we consider that, besides σ bond character, there is a certain π bond character in the three bonds.

In molecule XII, the Mo atom is coordinated by eight carbon atoms. Each of three CO ligands forms a σ-π bond with the Mo atom and provides a pair of bonding electrons. The two π molecular orbitals, corresponding to the C(14)–C(15) and C(17)–C(18) double bonds of bicycloheptadiene ligand, bond to the Mo atom and provide four electrons. That the sum of the three bond angles around C(4) atom is exactly 360° may indicate that the C(4) atom forms three σ bond with the adjacent three atoms using its sp^2 hybridized orbitals and a π bond with the Mo atoms using its pure P_z orbital, and provides two electrons to satisfy the 18-electron rule. If we see merely the six carbon atoms around the Mo atom (C(1), C(2), C(3), C(4), C(14) and C(18)), they construct an approximate octahedron. The distance between Mo atom and the equatorial plane is 0.2912 Å. The dihedral angles between the benzene ring and C(3)C(4)C(14)C(18) equatorial plane, and the benzene ring and C(4)C(5)O(4)Mo plane are 67° and 113°, respectively. The dihedral angle between the equatorial plane and the C(4)C(5)O(4)Mo plane is 93°.

Experimental

Preparation of complexes IV–XIII

IR, ^{1}H NMR and mass spectra were measured on Zeiss Specord-75 spectrophotometer, Varian XL-200 spectrometer and Finnigan 4021 GC/MS/DS spectrometer, reespectively.

All manipulations were carried out under purified N_2 atmosphere with standard Schlenk techniques. Pentane and petroleum ether (30 to 60 °C) were distilled from CaH_2, diethyl ether was distilled from sodium benzophenone ketyl, methylene chloride was distilled from P_2O_5 and purged with N_2. The alumina (neutral) used for chromatography was deoxygenated in a high vacuum, deactivated with 5% W/W water and stored under N_2. Cycloheptatriene(tricarbonyl)-molybdenum (I) [10] and -chromium (II) [11], bicycloheptadiene(tetracarbonyl)molybdenum (III) [12], Et_3OBF_4 [13] and aryllithium reagents [14–18] were prepared by literature methods.

1. $C_7H_8(CO)_2MoC(OC_2H_5)C_6H_5$ (IV). To a solution of 0.70 g (2.57 mmol) of I in 50 ml of ether was added dropwise 2.60 mmol of C_6H_5Li [14] in 20 ml of ether at −60 °C within 15 min. The reaction mixture changed gradually from orange to dark-red and an orange-red precipitate formed. The mixture was stirred at −50 °C for 3 h. After evaporation of solvent in a high vacuum, the orange-red solid residue was dissolved in 50 ml of N_2-saturated water at 0 °C and covered with pentane. Immediately afterwards Et_3OBF_4 [13] was added portionwise, with efficient stirring, to the aqueous solution until it became acidic. The aqueous solution was extracted with pentane and the extract was dried over anhydrous Na_2SO_4. After removal of solvent in vacuum, the residue was submitted to column chromatography on alumina at −20 °C with pentane followed by pentane/ether (10/1) as eluent. Removal of the solvent and recrystallization from pentane at −80 °C gave 0.50 g (51%, based on I) of orange-red crystals, m.p. 73–74 °C (decomp.). Found: C, 57.05; H, 4.89; Mo, 25.16. $C_{18}H_{18}O_3Mo$ (378.28) calcd.: C, 57.15; H, 4.80; Mo, 25.36%. Mol. wt. 378, 380 (mass spectroscopically, based on ^{96}Mo and ^{98}Mo, respectively).

2. $C_7H_8(CO)_2MoC(OC_2H_5)C_6H_4CH_3$-p (V). Similar to the procedures described in 1, the reaction of 0.60 g (2.2 mmol) of I with 2.2 mmol of *p*-$CH_3C_6H_4Li$ [15], followed by alkylation and further treatment gave 0.38 g (44%, based on I) of bright red crystals, m.p. 100–101 °C (decomp.). Found: C, 58.43; H, 5.43; Mo, 24.25. $C_{19}H_{20}O_3Mo$ (392.31) calcd.: C, 58.17; H, 5.14; Mo, 24.46%. Mol. wt. 394 (mass spectroscopically, based on ^{98}Mo).

3. $C_7H_8(CO)_2MoC(OC_2H_5)C_6H_4CH_3$-o (VI). The reaction of 0.80 g (2.9 mmol) of I with 2.9 mmol of *o*-$CH_3C_6H_4Li$ [15] in a similar manner as described in 1 gave orange-red crystals, m.p. 96–97 °C (decomp.), yield 0.43 g (37%, based on I). Found: C, 58.12; H, 5.03; Mo, 23.83. $C_{19}H_{20}O_3Mo$ (392.31) calcd.: C, 58.17; H, 5.14; Mo, 24.46%. Mol. wt. 394 (mass spectroscopically).

4. $C_7H_8(CO)_2MoC(OC_2H_5)C_6H_4CF_3$-p (VII). A solution of 2.2 mmol of n-C_4H_9Li [16] in 20 ml of ether was added dropwise to a solution of 0.50 g (2.2 mmol) of *p*-$CF_3C_6H_4Br$ in 20 ml of ether. After 20 min stirring at room temperature, the resulting solution of *p*-$CF_3C_6H_4Li$ [17] was allowed to react, analogously to 1, with 0.60 g (2.2 mmol) of I in 50 ml of ether at −60 °C. The crude products were recrystallized from pentane/CH_2Cl_2 (10/1) at −80 °C to give 0.40 g (41%, based on I) of dark-red needles, m.p. 107–108 °C (decomp.). Found: C, 51.21; H, 4.12; F, 12.54; Mo, 22.21. $C_{19}H_{17}O_3F_3Mo$(446.28) calcd: C, 51.14; H, 3.84; F, 12.77; Mo, 21.50%. Mol. wt. 448 (mass spectroscopically, based on ^{98}Mo).

5. $C_7H_8(CO)_2CrC(OC_2H_5)C_6H_4CF_3$*-p (VIII).* 0.60 g (2.6 mmol) of II was allowed to react with 2.6 mmol of fresh *p*-$CF_3C_6H_4Li$ as described above for IV to give 0.26 g (24%, based on II) of black crystals. Found: C, 56.48; H, 4.14; F, 14.20. $C_{19}H_{17}O_3F_3Cr$ (402.34) calcd.: C, 56.72; H, 4.26; F, 14.17%.

6. 7-exo-$(CH_3C_7H_7)Cr(CO)_3$. To a solution of 0.30 g (1.3 mmol) of II in 50 ml of ether was added dropwise 1.3 mmol of C_6H_5Li (or *p*-, *o*-$CH_3C_6H_4Li$) at −50 °C within 15 min. The mixture was allowed to warm to −30 °C and stirred at this temperature for 3 h. A red powder precipitated. The resulting mixture was cooled to −40 °C and excess CH_3I (15 equiv.) was added dropwise. A grey white precipitate (LiI) formed and the resulting solution darkened to red. After stirring at −30 °C for an hour, the solvent was removed in a high vacuum. The deep-red residue was chromatographed on alumina at −20 °C with pentane as eluant, which eluted a single red zone. After removal of solvent, the crude product was recrystallized from pentane at −80 °C to give 0.06 g (19%, based on II) of bright red needles, m.p. 83–84 °C (lit. [5] 85–85.5 °C). IR (ν(CO)): 1900vs, 1922vs, 1982vs cm^{-1}. ^{1}H NMR (acetone-d_6): δ 6.28 (2H, m), 5.0 (2H, m), 3.52 (2H, m), 1.74 (1H, m), 1.10 (3H, m) ppm. Mol. wt. 242 (mass spectroscopically).

7. $C_7H_8(CO)_3MoC(OC_2H_5)C_6H_5$ *(IX).* The reaction of 0.50 g (1.7 mmol) of III in 50 ml of ether with 2.5 mmol of C_6H_5Li at −60 to −50 °C for 3 h, followed by alkylation and further treatment similar to the procedures described in 1 gave 0.15 g (22%, based on III) of bright orange-red crystals, m.p. 68–70 °C (decomp.). Found: C, 56.09; H, 4.45. $C_{19}H_{18}O_4Mo$ (406.29) calcd.: C, 56.17; H, 4.46%. Mol. wt. 406, 208 (mass spectroscopically, based on ^{96}Mo and ^{98}Mo respectively).

8. $C_7H_8(CO)_3MoC(OC_2H_5)C_6H_4CH_3$*-m (X).* 0.40 g (1.3 mmol) of III was allowed to react as described for IV with 1.7 mmol of *m*-$CH_3C_6H_4Li$ [15] at −50 °C for 3 h to give 0.11 g (20%, based on III) of red crystals, m.p. 53–55 °C (decomp.). Found: C, 56.86; H, 4.91. $C_{20}H_{20}O_4Mo$ (420.31) calcd.: C, 57.15; H, 4.80%. Mol. wt. 420 (mass spectroscopically).

9. $C_7H_8(CO)_3MoC(OC_2H_5)C_6H_4CH_3$*-o (XI).* 0.30 g (1.0 mmol) of III was allowed to react with 1.4 mmol of *o*-$CH_3C_6H_4Li$ in ether at −60 to −40 °C for 3 h. The subsequent alkylation and treatment as described for IV gave orange-red crystals, yield 0.26 g (62%, based on III), m.p. 98 °C (decomp.). Found: C, 57.60; H, 4.85. $C_{20}H_{20}O_4Mo$ (420.31) calcd.: C, 57.15; H, 4.80%. Mol. wt. 420, 422 (mass spectroscopically).

10. $C_7H_8(CO)_3MoC(OC_2H_5)C_6H_4CH_3$*-p (XII).* 0.30 g (1.0 mmol) of III was allowed to react with 1.4 mmol of *p*-$CH_3C_6H_4Li$ as described above for IV to give 0.10 g (24%, based on III) of red crystals, m.p. 78 °C (decomp.). Found: C, 57.27; H, 4.92. $C_{20}H_{20}O_4Mo$ (420.31) calcd.: C, 57.15; H, 4.80%. Mol. wt. 420, 422 (mass spectroscopically).

11. $C_7H_8(CO)_3MoC(OC_2H_5)C_6H_4OCH_3$*-p (XIII).* A solution of 0.28 g (1.5 mmol) of *p*-$CH_3OC_6H_4Br$ in 20 ml of ether was mixed with 1.5 mmol of n-C_4H_9Li. After 20 min stirring at room temperature, the resulting ether solution of *p*-$CH_3OC_6H_4Li$ [18] was allowed to react, as described for IV, with 0.45 g (1.5 mmol) of III at −60 to −40 °C for 4 h to yield 0.08 g (12%, based on III) of orange

(Continued on p. 82)

Table 5

Atom coordinates ($\times 10^4$) and temperature factors ($\times 10^3$) for VI and XII

Atom	VI				XII			
	x	y	z	U_{eq}	x	y	z	U_{eq}
Mo	1409(1)	1350(1)	1672(1)	42(1)	1036(2)	1510(8)	7432.6(8)	62.6(4)
O(1)	−1091(8)	2578(3)	2445(4)	76(2)	−2027(20)	280(8)	7689(11)	103(6)
O(2)	−2352(8)	853(3)	266(4)	89(3)	3919(21)	2945(13)	7366(11)	127(7)
O(3)	2119(7)	1971(2)	−226(3)	60(2)	−1376(21)	2974(9)	6715(10)	111(6)
O(4)					1684(16)	2564(8)	8987(8)	79(4)
C(1)	−169(11)	2136(4)	2132(5)	54(3)	−1004(19)	672(10)	7600(14)	75(6)
C(2)	−955(11)	1032(4)	798(5)	58(3)	2941(23)	2416(11)	7397(12)	86(6)
C(3)	5003(11)	1200(4)	2175(5)	69(3)	−511(27)	2433(12)	6963(12)	81(7)
C(4)	4448(9)	1579(4)	2873(4)	59(3)	564(21)	2021(10)	8618(12)	67(5)
C(5)	3328(10)	1265(5)	3565(5)	91(4)	−981(21)	1838(10)	9146(9)	62(5)
C(6)	1503(11)	872(4)	3174(4)	64(3)	−2535(22)	2101(13)	8875(13)	78(6)
C(7)	1328(11)	286(4)	2550(5)	65(3)	3936(25)	1897(13)	9362(13)	86(6)
C(8)	2564(12)	128(4)	1901(5)	67(3)	−3815(22)	1369(13)	73(12)	82(6)
C(9)	4177(10)	551(4)	1712(4)	56(3)	2291(27)	1105(17)	294(14)	94(8)
C(10)	1911(8)	2067(4)	653(4)	41(2)	873(24)	1313(15)	9860(12)	88(7)
C(11)	2063(9)	2895(4)	796(4)	43(2)	−5380(33)	1088(19)	588(18)	188(10)
C(12)	3877(10)	3191(4)	1220(4)	53(3)	1269(26)	3132(15)	9694(13)	95(7)
C(13)	4109(11)	3965(4)	1346(4)	73(3)	2640(34)	3717(24)	9808(27)	184(18)
C(14)	2516(14)	4418(4)	1094(5)	85(4)	2190(27)	24(12)	7610(12)	90(7)
C(15)	733(14)	4137(4)	694(5)	78(4)	3555(22)	613(14)	7533(17)	90(7)
C(16)	469(11)	3367(4)	508(4)	55(3)	4017(22)	613(17)	6635(17)	101(8)
C(17)	−1518(10)	3078(5)	5(5)	87(4)	2555(22)	1104(13)	6194(10)	79(6)
C(18)	2104(12)	1224(4)	−616(5)	83(4)	1195(29)	500(12)	6295(10)	85(7)
C(19)	3014(12)	1245(5)	−1417(5)	87(4)	1908(34)	−307(13)	6711(3)	101(8)
C(20)					3673(31)	−342(18)	640(15)	126(11)

Table 6

Hydrogen coordinates ($\times 10^4$) and temperature factors ($\times 10^3$) for VI

Atom	x	y	z	U_{iso}
H(3)	6131	1401	1959	83
H(4)	4816	2098	2935	74
H(5)	2988	1673	3928	104
H(5)	4182	923	3956	104
H(6)	313	1032	3371	82
H(7)	244	−53	2554	77
H(8)	2267	−322	1548	79
H(9)	4779	377	1213	68
H(12)	4975	2861	1425	68
H(13)	5384	4170	1609	87
H(14)	2656	4947	1202	97
H(15)	−378	4470	534	88
H(17)	−2409	3496	−31	99
H(17)	−2016	2671	321	99
H(17)	−1413	2922	−607	99
H(18)	761	1049	−786	99
H(18)	2842	891	−167	99
H(19)	2907	751	−1676	104
H(19)	4388	1368	−1210	104
H(19)	2423	1599	−1878	104

Table 7

Bond lengths (Å) and bond angles (deg.) for VI

Mo–C(1)	1.968(8)	C(11)–C(12)	1.388(9)	C(3)–C(4)	1.346(10)
Mo–C(3)	2.452(7)	C(12)–C(13)	1.400(9)	C(4)–C(5)	1.497(11)
Mo–C(6)	2.362(7)	C(14)–C(15)	1.351(12)	C(6)–C(7)	1.383(10)
Mo–C(8)	2.324(7)	C(16)–C(17)	1.514(10)	C(8)–C(9)	1.410(11)
Mo–C(10)	2.053(6)	C(18)–C(19)	1.437(12)	C(10)–O(3)	1.342(7)
C(2)–O(2)	1.163(8)	Mo–C(2)	1.956(7)	C(11)–C(16)	1.382(9)
C(3)–C(9)	1.409(9)	Mo–C(4)	2.501(6)	C(13)–C(14)	1.345(11)
C(5)–C(6)	1.456(10)	Mo–C(7)	2.305(8)	C(15)–C(16)	1.408(10)
C(7)–C(8)	1.421(12)	Mo–C(9)	2.368(7)	O(3)–C(18)	1.451(9)
C(10)–C(11)	1.494(9)	C(1)–O(1)	1.161(9)		
C(1)–Mo–C(2)	89.6(3)	Mo–C(7)–C(6)	75.1(4)	C(6)–Mo–C(9)	83.1(2)
C(2)–Mo–C(3)	146.0(3)	C(6)–C(7)–C(8)	127.6(7)	C(8)–Mo–C(9)	35.0(3)
C(2)–Mo–C(4)	172.2(3)	Mo–C(8)–C(9)	74.2(4)	C(2)–Mo–C(10)	86.1(3)
C(1)–Mo–C(6)	81.6(3)	Mo–C(9)–C(3)	76.3(4)	C(4)–Mo–C(10)	100.6(2)
C(3)–Mo–C(6)	80.2(2)	C(3)–C(9)–C(8)	127.1(7)	C(7)–Mo–C(10)	161.9(3)
C(1)–Mo–C(7)	108.7(3)	Mo–C(10)–O(3)	133.6(4)	C(9)–Mo–C(10)	98.6(2)
C(3)–Mo–C(7)	82.5(3)	C(10)–C(11)–C(12)	118.3(5)	Mo–C(2)–O(2)	178.6(7)
C(6)–Mo–C(7)	34.4(3)	C(12)–C(11)–C(16)	119.8(6)	Mo–C(3)–C(9)	69.7(4)
C(2)–Mo–C(8)	92.3(3)	C(12)–C(13)–C(14)	119.2(7)	Mo–C(4)–C(3)	72.2(4)
C(4)–Mo–C(8)	80.5(2)	C(14)–C(15)–C(16)	121.3(8)	C(3)–C(4)–C(5)	126.1(6)
C(7)–Mo–C(8)	35.8(3)	C(11)–C(16)–C(17)	122.0(6)	Mo–C(6)–C(5)	93.8(5)
C(2)–Mo–C(9)	113.7(3)	C(10)–O(3)–C(18)	120.4(5)	C(5)–C(6)–C(7)	126.0(7)
C(4)–Mo–C(9)	61.5(2)	C(1)–Mo–C(3)	124.1(3)	Mo–C(7)–C(8)	72.9(4)
C(7)–Mo–C(9)	66.0(3)	C(1)–Mo–C(4)	94.5(2)	Mo–C(8)–C(7)	71.4(4)
C(1)–Mo–C(10)	89.2(3)	C(3)–Mo–C(4)	31.5(2)	C(7)–C(8)–C(9)	128.2(6)
C(3)–Mo–C(10)	89.5(2)	C(2)–Mo–C(6)	112.6(3)	Mo–C(9)–C(8)	70.8(4)
C(6)–Mo–C(10)	158.9(2)	C(4)–Mo–C(6)	61.6(2)	Mo–C(10)–C(11)	122.1(4)
C(8)–Mo–C(10)	126.3(3)	C(2)–Mo–C(7)	91.5(3)	C(11)–C(10)–O(3)	104.3(5)
Mo–C(1)–O(1)	176.4(6)	C(4)–Mo–C(7)	80.9(2)	C(10)–C(11)–C(16)	122.0(5)
Mo–C(3)–C(4)	76.3(4)	C(1)–Mo–C(8)	144.5(3)	C(11)–C(12)–C(13)	120.4(6)
C(4)–C(3)–C(9)	129.7(7)	C(3)–Mo–C(8)	63.7(3)	C(13)–C(14)–C(15)	121.1(7)
Mo–C(4)–C(5)	87.4(4)	C(6)–Mo–C(8)	64.9(3)	C(11)–C(16)–C(15)	118.1(6)
C(4)–C(5)–C(6)	115.1(6)	C(1)–Mo–C(9)	155.8(2)	C(15)–C(16)–C(17)	119.9(7)
Mo–C(6)–C(7)	70.5(4)	C(3)–Mo–C(9)	33.9(2)	O(3)–C(18)–C(19)	109.2(6)

Table 8

Bond lengths (Å) and bond angles (deg.) for XII

Mo–C(1)	2.07(2)	Mo–C(2)	2.03(2)	Mo–C(3)	1.99(2)
Mo–C(4)	2.06(4)	Mo–C(14)	2.42(2)	Mo–C(15)	2.42(2)
Mo–C(17)	2.39(2)	Mo–C(18)	2.36(2)	C(1)–O(1)	1.04(2)
C(2)–O(2)	1.11(3)	C(3)–O(3)	1.13(2)	C(4)–O(4)	1.34(2)
O(4)–C(12)	1.44(2)	C(12)–C(13)	1.41(4)	C(4)–C(5)	1.51(2)
C(5)–C(6)	1.37(2)	C(6)–C(7)	1.39(3)	C(7)–C(8)	1.38(3)
C(8)–C(9)	1.32(3)	C(9)–C(10)	1.36(3)	C(10)–C(5)	1.38(3)
C(8)–C(11)	1.55(3)	C(14)–C(15)	1.40(3)	C(15)–C(16)	1.47(3)
C(16)–C(17)	1.54(3)	C(16)–C(20)	1.50(2)	C(17)–C(18)	1.42(3)
C(18)–C(19)	1.49(3)	C(19)–C(14)	1.52	C(19)–C(20)	1.49(4)
C(1)–Mo–C(2)	172.6(9)	C(1)–Mo–C(3)	89.0(7)	C(1)–Mo–C(4)	87.5(7)
C(1)–Mo–C(14)	74.2(7)	C(1)–Mo–C(15)	107.9(6)	C(1)–Mo–C(17)	111.0(7)
C(1)–Mo–C(18)	76.2(8)	C(2)–Mo–C(3)	89.6(8)	C(2)–Mo–C(4)	85.2(7)
C(2)–Mo–C(14)	109.2(7)	C(2)–Mo–C(15)	75.5(7)	C(2)–Mo–C(17)	76.4(7)
C(2)–Mo–C(18)	111.2(7)	C(3)–Mo–C(4)	88.4(7)	C(3)–Mo–C(14)	155.9(7)
C(3)–Mo–C(15)	157.1(8)	C(3)–Mo–C(17)	100.6(7)	C(3)–Mo–C(18)	100.7(7)
C(4)–Mo–C(14)	107.6(7)	C(4)–Mo–C(15)	107.2(8)	C(4)–Mo–C(17)	159.3(6)
C(4)–Mo–C(18)	161.0(6)	C(14)–Mo–C(15)	33.8(7)	C(14)–Mo–C(17)	70.7(6)
C(14)–Mo–C(18)	59.0(6)	C(15)–Mo–C(17)	59.4(8)	C(15)–Mo–C(18)	69.7(8)
C(17)–Mo–C(18)	34.8(7)	O(1)–C(1)–Mo	177.0(2)	O(2)–C(2)–Mo	176.0(2)
O(3)–C(3)–Mo	176(2)	O(4)–C(4)–Mo	120(1)	C(5)–C(4)–Mo	126(1)
O(4)–C(4)–C(5)	114(2)	Mo–C(14)–C(19)	98(1)	C(19)–C(14)–C(15)	104(2)
Mo–C(14)–C(15)	73(1)	Mo–C(15)–C(14)	73(1)	Mo–C(15)–C(16)	98(1)
C(16)–C(15)–C(14)	106(2)	Mo–C(17)–C(18)	72(1)	Mo–C(17)–C(16)	98(1)
C(18)–C(17)–C(16)	103(2)	Mo–C(18)–C(19)	101(1)	Mo–C(18)–C(17)	74(1)
C(17)–C(18)–C(19)	105(2)	C(20)–C(16)–C(15)	101(1)	C(20)–C(16)–C(17)	102(2)
C(17)–C(16)–C(15)	105(2)	C(20)–C(19)–C(18)	104(2)	C(20)–C(19)–C(14)	100(2)
C(14)–C(19)–C(18)	103(2)	C(19)–C(20)–C(16)	93(2)		

needles, m.p. 72°C (decomp.). Found: C, 55.17; H, 4.33. $C_{20}H_{20}O_4Mo$ (436.31) calcd.: C, 55.05; H, 4.62%. Mol. wt. 436, 438 (mass spectroscopically).

X-ray data collection and structure solution of VI and XII

Crystal of $C_{19}H_{20}O_3Mo$ (VI) and $C_{20}H_{20}O_4Mo$ (XII) suitable for X-ray diffraction study were obtained by recrystallization from pentane solution at −80°C. A single crystal of approximate dimension of 0.28 × 0.28 × 0.76 mm for VI and 0.10 × 0.20 × 0.40 mm for XII were sealed in capillaries under N_2 atmosphere for X-ray study. Intensity data of 2671 and 1926 independent reflections, of which 1781 and 1847 were observable, were collected with a Syntex R_3 four-circle diffractometer using Mo-K_α radiation by $\theta/2\theta$ scan mode within the range $3° \leq 2\theta \leq 45°$ and $3° \leq 2\theta \leq 50°$ for VI and XII, respectively.

The data were corrected for Lorentz and polarization effects. An empirical absorption factor correction was also applied for VI and XII. The crystal data for VI: a 6.862(3), b 17.859(12), c 14.744(4) Å, β 100.88(3)°, V 1774.2 Å^3, $Z = 4$, D_c 1.47 g/cm^3, and space group C_{2h}^5-$P2_1/c$. The crystal data for XII: a 7.9575(9), b 14.905(2), c 15.840(4) Å, $\alpha = \beta = \gamma = 90°$, V 1878.5 Å^3, $Z = 4$, D_c 1.47 g/cm^3, and space group D_2^3-$P22_12_1$.

The structure of VI and XII were solved by Patterson-Fourier techniques using the SHELXTL program. The fractional coordinates of the Mo atom was determined by the Patterson method and all other non-hydrogen atoms were derived from the difference Fourier function. The hydrogen atoms were added by theoretical calculation. Block-diagonal matrix least-squares refinement gave final discrepancy index $R_w = 0.0408$ for VI with 1756 reflections and $R_w = 0.111$ for XII with 1800 reflections. The atomic fractional coordinates and equivalent isotropic temperature factors of non-hydrogen atoms for VI and XII, and isotropic parameters of hydrogen atoms for VI are given in Table 5 and 6, respectively. The bond lengths and angles for VI and XII are listed in Table 7 and 8, respectively.

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