

Syntheses, structures, and catalytic activity in Friedel–Crafts acylations of substituted tetramethylcyclopentadienyl molybdenum carbonyl complexes

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Abstract

Reactions of the substituted tetramethylcyclopentadienes $[C_5HMe_4R]$ $[R = {}^tBu$, Ph, $CH_2CH_2C(CH_3)_3]$ with $Mo(CO)_3(CH_3CN)_3$ in refluxing xylene gave a series of dinuclear molybdenum carbonyl complexes $[(\eta^5-C_5Me_4R)Mo(CO)_3]_2$ $[R = {}^tBu$ (1), Ph (2), $CH_2CH_2C(CH_3)_3$ (3)], $[(\eta^5-C_5Me^tBu)Mo(\mu-CO)_2]_2$ (4)], and $[(\eta^5-C_5Me_4)^tBu]_2Mo_2O_4(\mu-O)$ (5)], respectively. Complexes 1–5 were characterized by elemental analysis, IR, ¹H NMR, and ¹³C NMR spectroscopy. In addition, their crystal structures were determined by X-ray crystal diffraction analysis. The catalytic activities of complexes 1–3 in Friedel–Crafts acylation in the presence of *o*-chloranil has also been investigated; the reactions were achieved under mild conditions to give the corresponding products in moderate yields.

Introduction

Transition metal complexes are of considerable utility as catalysts in organic synthesis [1–6]. The ligands usually play a crucial role in the catalytic processes by fine-tuning the electronic and geometric properties of the complex. Cyclopentadienyls have been among the most important ligands in organo-transition metal chemistry, as they form a wide range of derivatives whose steric and electronic properties can be easily tailored by varying the ring substituents. These variations on the cyclopentadienyl unit not only open access to

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new compounds, but also have great influence on the metallocene catalytic activity [7, 8].

The Friedel-Crafts reaction is well known and widely used for the production of value-added aromatic compounds through the formation of new C-C bonds. Conventional Friedel-Crafts alkylations are catalyzed by Lewis and Brönsted acids. However, the separation and handling of the acid waste in these homogeneous processes raise undesirable economic, environmental, and safety issues [9-18]. Therefore, considerable effort has been devoted to the development of environmentally friendly alternatives. Our laboratory has been pursuing the development of new ecofriendly catalyst systems. The activities and selectivities of different catalysts have been evaluated in our laboratory with a view to the development of green Friedel-Crafts acylation and alkylation reactions [19–24]. To obtain a deeper insight into the steric and electric effects of substituents on the molecular structures and reactions of the corresponding biscyclopentadienyl binuclear metal carbonyl complexes, we have now prepared a series of biscyclopentadienyl dimolybdenum complexes and determined their structures. The catalytic activities of the dinuclear molybdenum carbonyl complexes for Friedel-Crafts acylation have been investigated in the presence of o-chloranil as the oxidant. The results of our studies are presented in this paper.

Experimental

General considerations

All reactions were carried out under an argon/vacuum manifold using standard Schlenk techniques, except where noted otherwise. Solvents were distilled from appropriate drying agents under a dry argon atmosphere. ¹H and ¹³C NMR spectra were recorded on Bruker AV 500 or WIPM-NMR-400 spectrometers in CDCl₃, while IR spectra were recorded as KBr disks on an IR FT 8900 spectrometer. Gas chromatography was performed with an Agilent 6820 gas chromatography instrument. Mass spectra were recorded on a DSQ(II) gas chromatograph–mass spectrometer. The proligands [C₅Me₄HR] [R = ^{*i*}Bu, Ph, CH₂CH₂C(CH₃)₃] were prepared as described in the literature [25, 26]. Mo(CO)₃(CH₃CN)₃ was synthesized according to the literature procedure [27].

Synthesis of complex (1)

Under an argon atmosphere, a solution of $C_5HMe_4^{t}Bu$ (0.708 g, 4 mmol) and Mo(CO)₃(CH₃CN)₃ (2 mmol) in xylene (30 mL) was refluxed for 4 h. After removal of solvent, the residue was loaded onto an alumina column. Upon elution with petroleum ether/CH₂Cl₂ (10:1), a brown band was collected. After concentration, $[(\eta^5-C_5Me_4^{t}Bu)Mo(CO)_3]_2$ (1) was afforded as brown crystals. Yield: 36.8% (0.263 g). M.P: 174.9–175.8 °C; Anal. Calcd for $C_{32}H_{42}Mo_2O_6$: C, 53.78; H, 5.92. Found (%): C, 53.98; H, 5.94; ¹H NMR (CDCl₃, 400 MHz): δ 1.44 (s, 18H, CH₃), 1.81(s, 12H, C₅Me₄), 2.14 (s, 12H, C₅Me₄); ¹³C NMR (CDCl₃, 101 MHz): δ 11.2, 14.3, 32.5, 35.2, 102.1, 110.8, 114.9, 235.9. IR(v_{CO} , KBr, cm⁻¹): 1926(s), 1889(s), 1870(s).

Synthesis of complex (2)

Using a procedure similar to that described above, C_5HMe_4Ph was reacted with $Mo(CO)_3(CH_3CN)_3$ in refluxing xylene for 48 h. After chromatography and elution with petroleum ether, $[(\eta^5-C_5Me_4Ph)Mo(CO)_3]_2$ (2) was obtained (0.38 g, 28.6% yield) as dark red crystals. M.P. 136.3–137.0 °C; Anal. Calcd for $C_{36}H_{34}Mo_2O_6$: C, 57.31; H, 4.54. Found (%): C, 56.87; H, 4.15; ¹H NMR (CDCl₃, 500 MHz): δ 1.92 (s, 12H, C_5Me_2), 2.01 (s, 12H, C_5Me_2), 7.28–7.36 (m, 10H, C_6H_5); ¹³C NMR (CDCl₃, 101 MHz): δ 9.9, 10.6, 103.5, 104.9, 109.6, 127.2, 128.0, 131.4, 132.9, 238.8. IR(v_{CO} , KBr, cm⁻¹): 1869(s), 1822(s).

Synthesis of complex (3)

Using a procedure similar to that described above, $C_5HMe_4CH_2CH_2C(CH_3)_3$ was reacted with $Mo(CO)_3(CH_3CN)_3$ in refluxing xylene for 48 h. After chromatography and elution with petroleum ether, $[(\eta^5-C_5Me_4CH_2CH_2C(CH_3)_3)]Mo(CO)_3]_2$ (3) was obtained (0.49 g, 31.7% yield) as dark red crystals. M.P. 135.4–135.8 °C; Anal. Calcd for $C_{36}H_{50}Mo_2O_6$: C, 56.11; H, 6.54. Found (%): C, 56.33; H, 6.56; ¹H NMR (CDCl₃, 500 MHz): δ 0.92 (s, 18H, CH₃), 1.14–1.18 (m, 4H, CH₂), 1.94(s, 24H, C₅Me₄), 2.27–2.31 (m, 4H, CH₂); ¹³C NMR (CDCl₃, 125 MHz): δ 10.4, 10.7, 21.0, 29.0, 30.6, 44.8, 104.0, 105.1, 109.4, 235.5. IR(v_{CO} , KBr, cm⁻¹): 1921(s), 1888(s), 1871(s).

Synthesis of complex (4)

Using a procedure similar to that described above, $C_5HMe_4^tBu$ was reacted with $Mo(CO)_3(CH_3CN)_3$ in refluxing xylene for 12 h. After chromatography and elution with petroleum ether, $[(\eta^5-C_5Me^tBu)Mo(CO)_4Mo(\eta^5-C_5Me_4^tBu)]$ (4) was obtained (0.61 g, 46.9% yield) as dark red crystals. M.P. 166.7–167.5 °C; Anal. Calcd for $C_{30}H_{42}Mo_2O_4$: C, 54.72; H, 6.42. Found (%): C, 54.67; H, 6.10; ¹H NMR (CDCl₃, 500 MHz): δ 1.92 (s, 12H, C_5Me_2), 2.04 (s, 12H, C_5Me_2), 1.37(s, 18H, ^tBu); ¹³C NMR (CDCl₃, 125 MHz): δ 10.3, 13.4, 32.7, 34.5, 102.8, 105.5, 115.7. IR (v_{CO} , KBr, cm⁻¹): 1867(s), 1826(s).

Synthesis of complex (5)

A solution of $C_5HMe_4^rBu$ (0.708 g, 4 mmol) and $Mo(CO)_3(CH_3CN)_3$ (2 mmol) in xylene (20 mL) was refluxed for 12 h under air. After chromatography and elution with petroleum ether, $[(\eta^5-C_5Me_4)'Bu]_2Mo_2O_4(\mu-O)]$ (5) was obtained (0.346 g, 27.6% yield) as dark red crystals. M.P. 159.6–160.5 °C; Anal. Calcd for $C_{26}H_{42}Mo_2O_5$: C, 49.85; H, 6.76. Found: C, 50.05; H, 6.78; ¹H NMR (DMSO, 400 MHz): δ 1.89 (s, 12H, C₅Me₂), 2.13 (s, 12H, C₅Me₂), 1.29 (s, 18H, C_5'Bu); ¹³C NMR (DMSO, 101 MHz): δ 10.8, 14.3, 31.6, 35.6, 122.1, 124.8, 127.4; IR (KBr, cm⁻¹): 908 w, 878 w ($v_{Mo=O}$), 761 w ($v_{Mo-O-Mo}$).

Crystallographic studies

Single crystals of complexes 1-5 suitable for X-ray diffraction were obtained from the slow evaporation of hexanedichloromethane solutions. All X-ray crystallographic data were collected on a Bruker AXS SMART 1000 CCD diffractometer, using graphite monochromated Mo *Ka* radiation

Table 1	Crystal data and	structure refinement	parameters for	complexes 1-5
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Complex	1	2	3	4	5
Empirical formula	C ₃₂ H ₄₂ Mo ₂ O ₆	C ₁₈ H ₁₇ MoO ₃	C ₃₆ H ₅₀ Mo ₂ O ₆	C ₃₀ H ₄₂ Mo ₂ O ₄	C ₂₆ H ₄₂ Mo ₂ O ₅
Formula weight	714.54	377.26	770.64	658.51	626.48
Temperature (K)	298 (2)	298 (2)	298 (2)	298 (2)	298 (2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system,	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P - 1	Pī	<i>P</i> 2(1)/c	$P2_1/n$	P2(1)/n
a (Å)	8.7635 (8)	8.8032 (7)	8.9750 (8)	8.3600 (15)	8.3263 (17)
<i>b</i> (Å)	12.0465 (12)	9.0574 (8)	16.2189 (14)	22.228 (4)	10.523 (2)
<i>c</i> (Å)	15.9764 (14)	11.7046 (9)	12.7041 (11)	15.872 (3)	15.401 (3)
<i>α</i> (°)	84.536 (2)	111.183 (3)	90	90	90
β (°)	87.952 (2)	107.893 (2)	91.0220 (10)	92.452 (2)	99.667 (2)
γ (°)	69.8520 (10)	90.9170(10)	90	90	90
Volume (Å ³)	1576.2 (3)	819.58 (12)	1849.0 (3)	2946.7 (9)	1330.3 (5)
Ζ	2	2	4	4	2
$D_{\text{calc}} (\text{g cm}^{-3})$	1.506	1.529	1.384	1.484	1.564
$\mu (\text{mm}^{-1})$	0.836	0.809	0.718	0.883	0.975
<i>F</i> (000)	732	382	796	1352	644
Crystal size(mm)	$0.18\times0.17\times0.14$	$0.40 \times 0.37 \times 0.26$	$0.38\times0.17\times0.15$	$0.45\times0.44\times0.40$	$0.20\times0.15\times0.14$
θ range (°)	2.48-25.02	2.44-25.02	2.51-25.02	2.57-25.02	2.35-25.01
Reflections collected	8042/5485	4157/2832	9148/3247	14,627/5173	6494/2348
R (int)	0.0210	0.0557	0.0333	0.0296	0.0211
Completeness to θ (%)	98.4	98.10	99.3	97.2	100.0
Absorption correction	Semi-empirical from	equivalents			
Max. and min. transmission	0.8919/0.8641	0.8132/0.7379	0.8999/0.7720	0.7191/0.6922	0.8755/0.8288
Refinement method	Full-matrix least-squ	ares on F^2			
Data/restraints/parameters	5485/0/361	2832/0/203	3247/0/206	5173/3/410	2348/0/158
Goodness-of-fit on F^2	1.021	1.073	1.072	1.078	1.309
R_1 , w $R_2[I > 2\sigma(I)]$	0.0342, 0.0851	0.0578, 0.1556	0.0321, 0.0636	0.0435, 0.1010	0.0253, 0.0603
R_1 , w R_2 (all data)	0.0500, 0.0899	0.0633, 0.1642	0.0564, 0.0742	0.0787, 0.1257	0.0364, 0.0668
Max. peak/(e Å ⁻³)	0.584	1.060	0.784	0.748	0.504
Mini. peak/(e Å ⁻³)	- 0.394	- 0.826	- 0.477	- 1.566	- 0.336
CCDC	1,574,536	1,555,752	1,559,899	1,556,542	1,565,792

 $(\varphi/\omega \text{ scan}, \lambda = 0.71073 \text{ Å})$. Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were done using the SHELXL-97 program system. Crystallographic data and experimental details of the structure determinations are given in Table 1. CCDC: 1574536, 1555752, 1559899, 1556542, and 1565792 for 1–5, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk.

General procedure for catalytic tests

Under an argon atmosphere, the required molybdenum carbonyl complex (0.2 mmol) and *o*-chloranil (0.8 mmol)

were mixed with 1,2-dichloroethane (3.5 mL) in a 25 mL round-bottom flask at room temperature. The solution was immediately darkened. After stirring for 40 min at room temperature, the aromatic compound (2 mmol) and acylating reagent (6 mmol) were added by syringe. The reaction mixture was then heated on an oil bath at 80 °C for 24 h. After cooling to room temperature, the solvent was removed through rotary evaporation. The residue was purified by Al_2O_3 column chromatography. Elution with petroleum ether/ethyl acetate (4:1, *V/V*) developed a colorless liquid that afforded the corresponding product. The course of the reaction was monitored using an Agilent 6820 gas chromatograph.

Results and discussion

Reactions of proligands $[C_5HMe_4R]$ with Mo(CO)₃(CH₃CN)₃

Treatment of the proligands $[C_5HMe_4R]$ $[R = {}^{t}Bu$, Ph, or $CH_2CH_2C(CH_3)_3]$ with $Mo(CO)_3(CH_3CN)_3$ in refluxing xylene under argon afforded the expected Mo–Mo singlebonded dinuclear complexes $[(\eta^5-C_5Me_4R)Mo(CO)_3]_2$ $[R = {}^{t}Bu$ (1), Ph (2), $CH_2CH_2C(CH_3)_3$ (3)] (Scheme 1). Among the three reactions, the *t*-butyl-substituted proligand gave the shortest reaction time and highest activity, indicating that the steric and electronic effects of the substituent have a significant effect on the reaction.

The IR spectra of complexes 1-3 are similar; all show strong terminal carbonyl absorptions at 1926–1822 cm⁻¹. The ¹H NMR spectra of **1** and **2** are also similar, showing two singlets for the four methyl group protons, while the ¹H NMR spectrum of complex **3** shows one singlet for the four methyl group protons.

In order to further study the effect of substituent on the reaction, the reaction time for the reaction of $[C_5HMe_4 \ ^{t}Bu]$ with Mo(CO)₃(CH₃CN)₃ was extended. When the proligand $[C_5HMe_4^tBu]$ was reacted with $Mo(CO)_3(CH_3CN)_3$ in refluxing xylene for 12 h under an argon atmosphere, the unexpected Mo–Mo triple-bonded complex $[(\eta^5-C_5Me^tBu)Mo(CO)_4Mo(\eta^5-C_5Me_4^tBu)$ (4)] was obtained (Scheme 2). The IR spectrum of complex 4 showed characteristic strong absorption peaks for CO in the bridging v(CO) region, while the ¹H NMR spectrum showed two singlets for the four methyl group protons and one singlet for the *t*-butyl protons.

However, when proligand $[C_5HMe_4^tBu]$ was reacted with Mo(CO)₃(CH₃CN)₃ in refluxing xylene for 12 h while exposed to air, the dinuclear oxo-bridged complex $[(\eta^5-C_5Me_4)^tBu]_2Mo_2O_4(\mu-O)$ (5)] was obtained (Scheme 3). The IR spectrum of complex 5 shows three characteristic peaks at 908, 878, and 761 cm⁻¹, corresponding to the two terminal Mo=O stretching modes and a bridging antisymmetric Mo–O–Mo stretching mode, respectively. The ¹H NMR spectrum shows two singlets for the four methyl group protons and one singlet for the *t*-butyl protons.



Scheme 1 Synthesis of complexes 1–3. $R = {}^{t}Bu$ (1), Ph (2), $CH_2CH_2C(CH_3)_3$ (3)



Scheme 2 Synthesis of complex 4

Scheme 3 Synthesis of complex 5



Table 2	Selected bond distances (Å) and angles (°) for complexes 1 5
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1		2		3		4		5	
Bond distances	5								
Mo(1)–C(1)	2.344 (4)	Mo(1)-C(1)	2.329 (5)	Mo(1)-C(1)	2.414 (3)	Mo(1)-C(1)	2.338 (4)	Mo(1)–C(1)	2.361 (3)
Mo(1)–C(2)	2.320 (4)	Mo(1)–C(2)	2.326 (5)	Mo(1)–C(2)	2.378 (3)	Mo(1)-C(2)	2.337 (5)	Mo(1)–C(2)	2.451 (3)
Mo(1)–C(3)	2.387 (4)	Mo(1)-C(3)	2.385 (5)	Mo(1)-C(3)	2.312 (3)	Mo(1)-C(3)	2.355 (5)	Mo(1)–C(3)	2.481 (3)
Mo(1)–C(4)	2.424 (4)	Mo(1)–C(4)	2.423 (5)	Mo(1)–C(4)	2.300 (3)	Mo(1)-C(4)	2.352 (5)	Mo(1)–C(4)	2.475 (3)
Mo(1)–C(5)	2.384 (4)	Mo(1)-C(5)	2.380 (5)	Mo(1)–C(5)	2.373 (4)	Mo(1)-C(5)	2.326 (5)	Mo(1)-C(5)	2.430 (3)
Mo(1)-C(14)	1.989 (5)	Mo(1)-C(16)	1.958 (5)	Mo(1)-C(16)	1.973 (4)	Mo(1)-C(27)	2.127 (13)	Mo(1)–O(1)	1.8933 (4)
O(1)–C(14)	1.161 (5)	Mo(1)-C(17)	1.996 (6)	Mo(1)-C(17)	1.976 (5)	Mo(2)-C(28)	2.072 (10)	Mo(1)–O(2)	1.704 (2)
Mo(1)– Mo(1i)	3.3352 (7)	O(1)-C(16)	1.157 (7)	O(1)-C(16)	1.152 (4)	O(1)-C(27)	1.232 (12)	Mo(1)–O(3)	1.705 (2)
Mo(2)– Mo(2i)	3.3398 (7)	Mo(1)- Mo(1i)	3.309	Mo(1)- Mo(1i)	3.279	Mo(1)-Mo(2)	2.4775 (7)	O(1)-Mo(1i)	1.8933 (4)
Bond angles									
C(2)-Mo(1)- C(1)	36.36 (12)	C(2)–Mo(1)– C(1)	36.19 (17)	C(2)–Mo(1)– C(1)	34.55 (11)	C(2)–Mo(1)– C(1)	35.85 (17)	C(2)-Mo(1)- C(1)	34.99 (9)
C(3)–Mo(1)– C(4)	34.30 (12)	C(3)–Mo(1)– C(4)	34.60 (17)	C(3)–Mo(1)– C(4)	36.11 (12)	C(3)–Mo(1)– C(4)	34.60 (18)	C(3)-Mo(1)- C(4)	33.37 (10)
C(1)–Mo(1)– C(3)	59.21 (12)	C(1)–Mo(1)– C(3)	59.00 (18)	C(1)–Mo(1)– C(3)	58.24 (11)	C(1)–Mo(1)– C(3)	59.27 (16)	C(1)-Mo(1)- C(3)	56.84 (9)
C(15)- Mo(1)- C(14)	77.45 (19)	C(16)– Mo(1)– C(17)	77.0 (2)	C(16)– Mo(1)– C(17)	77.85 (15)	C(27)– Mo(1)– C(29)	118.7 (5)	O(2)-Mo(1)- O(1)	105.38(9)
C(15)- Mo(1)- C(16)	76.3 (2)	C(16)– Mo(1)– C(18)	77.5 (2)	C(16)– Mo(1)– C(18)	77.34(16)	C(28)– Mo(2)– C(29)	83.8(5)	O(2)-Mo(1)- O(3)	105.78 (14)
C(16)– Mo(1)– C(14)	112.09 (19)	C(18)– Mo(1)– C(17)	110.0 (2)	C(18)– Mo(1)– C(17)	111.93 (15)	C(28)- Mo(2)- Mo(1)	68.8 (3)	Mo(1)-O(1)- Mo(1i)	180.000 (15)

Crystal structures

The crystal structures of complexes 1-5 were determined by X-ray diffraction. Selected bond parameters for these complexes are presented in Table 2. The structures of complexes 1-3 are shown in Figs. 1, 2, and 3. All three complexes consist of two $(C_5Me_4R)Mo(CO)_3$ units, in which each of the molybdenum atoms is coordinated with an η^5 -cyclopentadienyl and three terminal CO ligands. All the complexes are disposed in the trans conformation and linked by an Mo-Mo bond, such that the structures lie on a crystallographic inversion. Two structurally independent but chemically equivalent molecules are present in the unit cell. The fifth coordination position is occupied by a cyclopentadienyl ring that is essentially planar. For complex 1, the unit cell contains two environmentally different molecules Mo(1) and Mo(2), which have the same basic structure, but small differences in some bond lengths and angles. The Mo-Mo distances are 3.3352 (7) and 3.3398 (7) Å, respectively. Although there are two distinct molecules in the unit cell, the ¹H NMR spectrum of **1** shows only one. This indicates that complex 1 may exist as one form in solution; however, the possibility of a rapid fluxional process cannot be excluded. For complex 2, the conformation of the phenyl substituent is found to be a regular hexagon. The structural parameters of complexes 1-3 are very similar to those in other $[\eta^5-C_5H_4RMo(CO)_3]_2$ complexes; the Mo-Mo bond distances are [3.3352 (7) and 3.3398 (7) Å for complex (1)], 3.309 Å for (2) and 3.279 Å for (3), which are comparable to other metal-metal bond distances found in this kind of $[\eta^5 - C_5 Me_4 RMo(CO)_3]_2$ complex [R = PhMe,(3.283 Å); R = PhOMe (3.307 Å) [28]; R = benzyl (3.266 Å)[29]; R = n-butyl (3.286 Å) [30]]. However, the Mo–Mo bond distances for complexes 1-3 are longer than those reported for *trans*- $[\eta^5$ -C₅H₅Mo(CO)₃]₂ [3.235(1) Å] [31] and $[\eta^5 - C_5 H_4^i Pr Mo(CO)_3]_2$ [3.222(5) Å] [32], suggesting that the substituents of the cyclopentadienyl ring have different degrees of steric hindrance.

The molecular structure of complex **4** is shown in Fig. 4. The molecule consists of two *t*-butyl-substituted tetramethylcyclopentadienyl molybdenum moieties symmetrically bridged by four carbonyls. Complex **4** is a *cis*-dimolybdenum complex, in which every molybdenum atom is coordinated by an η^5 -cyclopentadienyl and four



Fig. 1 Molecular structure of 1 with atom numbering scheme. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity. Mo1-Mo1i = 3.3352(7) Å, Mo2-Mo2ii = 3.3398(7) Å





bridging carbonyl ligands. According to the EAN formalism, a triple Mo–Mo bond must be formulated, which is in agreement with the very short intermetallic length, 2.4777 (8) Å, ca. 0.8 Å shorter than the corresponding distance in the electron-precise complexes **1–3** and similar to the values found for related triply bonded cyclopentadienyl complexes bridged by dialkyl- or diarylphosphide ligands such as $[Mo_2Cp_2(\mu-COEt)-(\mu-PCy_2)(\mu-CO)]$ (2.478(1) Å) [33], $[Mo_2Cp_2(\mu-PPh_2)_2(\mu-CO)]$ (2.515(2) Å) [34], and $[Mo_2Cp_2(\mu-PhPC_6H_4PPh)_2(\mu-CO)]$ (2.532(1) Å) [35]. We should note that complex **4** is the first example of a complex having four carbonyl ligands bridging a triple metal-metal bond discovered in our laboratory.

The molecular structure of complex 5 is shown in Fig. 5. Complex 5 is a pentaoxo dimer and crystallizes in the monoclinic space group P2(1)/n. The molecule contains two molybdenum atoms connected with a single oxygen bridge. The two cyclopentadienyl planes are parallel. The complex is centrosymmetric with a Mo(1)–O(1)–Mo(1i) angle of 180°; the Mo(1)–O(1)–Mo(1i) moiety is collinear. This linear arrangement is attributed to π -bonding after the possible consequences of steric interactions are considered. In fact, a Fig. 3 Molecular structure of 3 with atom numbering scheme. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity. Mo1–Mo1i = 3.279 Å



Fig. 4 Molecular structure of **4** with atom numbering scheme. Thermal ellipsoids are shown at the 10% level. Hydrogen atoms are omitted for clarity



linear, centrosymmetric arrangement in a $[(MoO_2)_2O]$ unit has been previously observed in $[(\eta^5-C_5Me_5)MoO_2]_2(\mu-O)$ [36]. In complex 5, the bond distances of Mo(1)–O(1) and Mo(1i)–O(1) are identical [1.8933 (4) Å], while the terminal Mo=O distances (average 1.7045 Å) are much longer than those in $[(\eta^5-C_5Me_5)MoO_2]_2(\mu$ -O) (average 1.67 Å)]. The



Scheme 4 Complexes 1–3/*o*-chloranil-catalyzed Friedel–Crafts acylation reactions of toluene/anisole with acyl chlorides. $R_1 = OCH_3(6)$, $CH_3(7)$; $R_2 = Ph(a)$, $PhCH_2(b)$, $c-C_6H_{11}(c)$, $n-C_5H_{11}(d)$, PhCH=CH(e)



Scheme 5 Complexes 1–3/o-chloranil-catalyzed Friedel–Crafts acylation reactions of anisole derivatives with acyl chlorides. $R_1 = H$; $R_2 = CH_3(8)$, Br(9). $R_1 = CH_3(10)$, Br(11); $R_2 = H$. $R_3 = Ph$ (a), $PhCH_2$ (b), $c-C_6H_{11}$ (c), $n-C_5H_{11}$ (d), PhCH=CH (e)

long bond distances of terminal Mo=O bonds have been suggested to decrease O–O repulsion and result in O–Mo–O angles larger than 90°.

Catalytic studies

In order to test the ability of these complexes to catalyze Friedel–Crafts acylation reactions (Schemes 4, 5), influencing factors such as the reaction time, yield, and economic considerations were initially considered. The influence of quinones on catalytic efficacy has been discussed by Yamamoto et al. [37]. *o*-Chloranil was identified as the best oxidant. The optimized experimental conditions were as follows: 1,2-dichloroethane as solvent; a molar ratio 1:3 of aromatic substrate and acylation reagent; the amount of catalyst was 10 mol% (substrate as reference); the molar ratio of catalyst to oxidant was 1:4; reaction temperature 80 °C, reaction time 24 h.

Table 3Catalytic data ofcomplexes 1–3

Aromatic substrate	Reagent	Yield [%] cata- lyzed by 1	Yield [%] cata- lyzed by 2	Yield [%] catalyzed by 3
PhMe	PhCOCl	56.5	58.7	55.2
	PhCH ₂ COCl	44.8	45.6	45.1
	<i>n</i> -C ₅ H ₁₁ COCl	-	-	31.5
	c-C ₆ H ₁₁ COCl	28.3	30.8	-
	PhCH=CHCOCl	-	_	_
PhOMe	PhCOCl	79.7	82.3	83.5
	PhCH ₂ COCl	66.5	71.8	68.4
	<i>n</i> -C ₅ H ₁₁ COCl	28.8	29.8	58.3
	c-C ₆ H ₁₁ COCl	57.9	58.1	28.6
	PhCH=CHCOCl	55.1	55.7	55.7
o-C ₆ H ₄ (Me)(OMe)	PhCOCl	86.9	87.4	88.2
	PhCH ₂ COCl	71.8	72.6	62.4
	<i>n</i> -C ₅ H ₁₁ COCl	28.5	29.7	78.8
	c-C ₆ H ₁₁ COCl	76.5	79.6	32.3
	PhCH=CHCOCl	48.3	58.4	58.5
o-C ₆ H ₄ (Br)(OMe)	PhCOCl	66.1	67.7	62.3
	PhCH ₂ COCl	55.6	57.1	56.7
	<i>n</i> -C ₅ H ₁₁ COCl	27.1	27.5	54.5
	c-C ₆ H ₁₁ COCl	57.7	58.8	28.6
	PhCH=CHCOCl	29.2	32.8	28.7
$p-C_6H_4(Me)(OMe)$	PhCOCl	43.1	57.6	56.5
	PhCH ₂ COCl	29.6	31.3	30.1
	<i>n</i> -C ₅ H ₁₁ COCl	3.6	6.4	14.5
	c-C ₆ H ₁₁ COCl	16.1	18.7	4.8
	PhCH=CHCOCl	10.4	12.5	11.8
$p-C_6H_4(Br)(OMe)$	PhCOCl	31.4	26.3	31.7
	PhCH ₂ COCl	24.6	25.4	25.3
	<i>n</i> -C ₅ H ₁₁ COCl	-	_	_
	c-C ₆ H ₁₁ COCl	-	-	-
	PhCH=CHCOCl	_	-	-

Reagents and conditions: benzene derivatives: 2 mmol, acylating reagents: 6 mmol, $[Cp*Mo(CO)_3]_2$: 10 mol%, *o*-chloranil 40 mol%, 80 °C, 24 h

- no product detected

Complexes 1–3 all proved to be capable of catalyzing Friedel–Crafts acylation reactions. The yields were found to vary with the different catalysts used, as indicated in Table 3. The catalytic results for the three complexes were all basically similar; the different substituents have only a small influence on the catalytic behavior. Since these substituents were not directly coordinated with the metal atoms, their electronic and steric effects are probably limited. The aryl products were obtained in moderate yields, with high *para*-selectivities. The pattern of results suggests that the reactions proceed by an electrophilic substitution mechanism. Benzoyl chloride, phenylacetyl chloride, cyclohexyl chloride, and cinnamyl chloride could all be used as acylating reagents in these reactions. Comparing 2-methyl anisole as the substrate and catalytic yield as standard, the order of

reactivity of the different acylating reagents was found to be: benzoyl chloride > phenylacetyl chloride > cyclohexanoyl chloride > cinnamyl chloride > hexanoyl chloride.

Conclusions

Reactions of substituted tetramethylcyclopentadienes with $Mo(CO)_3(CH_3CN)_3$ provided a series of substituted tetramethylcyclopentadienyl dinuclear molybdenum carbonyl complexes. Friedel–Crafts reactions of aromatic compounds with a variety of acylation reagents showed that complexes 1–3 all have catalytic activity. Benzoyl chloride, phenylacetyl chloride, cyclohexyl chloride, and cinnamyl chloride could all be used as acylating reagents in these aromatic electrophilic substitution reactions. Compared with traditional catalysts, the present system has several practical advantages: lower amounts of catalysts, mild reaction conditions, high selectivity, and ease of use. To elucidate the reaction mechanism and expand the synthetic utility of these catalysts, further studies are currently in progress.

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