Transition Metal Chemistry
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Syntheses, structures and catalytic activities of molybdenum carbonyl complexes based on pyridine-imine ligands

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Abstract
Thermal treatment of pyridine imines [C_5H_4N-2-C(H)=N-C_6H_4-R] [R = H (**1**), CH_3 (**2**), OMe (**3**), CF_3 (**4**), Cl (**5**), Br (**6**)] with $Mo(CO)_6$ in refluxing toluene provided six novel mononuclear molybdenum carbonyl complexes of the type [(η^2-2-C_5H_4N)CH=N(C_6H_4-4-R)]$Mo(CO)_4$ [R = H (**7**); CH_3 (**8**); OMe (**9**); CF_3 (**10**); Cl (**11**); Br (**12**)]. All of these complexes were separated by chromatography and fully characterized by elemental analysis, IR, and NMR spectroscopy. The crystal structures of complexes **7**, **8** and **10** were determined by X-ray crystal diffraction analysis. In addition, the catalytic performance of these complexes was also tested, and it was found that these complexes had obvious catalytic activity on Friedel–Crafts reactions of aromatic compounds with a variety of acylation reagents.

Introduction

Transition metal carbonyl complexes play an important role in organometallic chemistry and are widely used as catalysts or catalyst precursors. Schiff bases are one of the most prevalent ancillary ligands in organometallic chemistry. Their metal complexes have a variety of biological, medicinal and analytical applications, in addition to their important roles in catalysis and organic syntheses [1–9]. Schiff bases which have oxygen and nitrogen donor atoms operate as good chelating agents for both transition and non-transition metals [10–13].

The direct C-acylation of aromatic compounds to form a new C–C bond was reported as early as 1873 [14] and provided the basis for one of the most famous name reactions in organic chemistry: the Friedel–Crafts acylation [15]. More than fourteen decades later, this approach for forming C–C bonds endures as the standard method to prepare a broad range of aromatic ketones, and especially C-acylated phenols [16, 17], by employing various types of catalysts [18, 19].

Our group have reported the synthesis and catalytic activity of a series of metal carbonyl complexes, showing that these metal carbonyl complexes have catalytic activity for Friedel–Crafts reactions [20–25]. Herein, we are presenting the synthesis and characterization of a series of new molybdenum carbonyl complexes bearing pyridine imines as chelating ligands. The properties of these complexes can be readily modified by substituent variations influencing both the electronic structure and the steric constraints around the central metal carbonyl motif. Furthermore, the catalytic reactivity of these mononuclear molybdenum carbonyl complexes for Friedel–Crafts acylation was also studied.

Results and discussion

Reactions of ligand precursors [C_5H_4N-2-C(H)=N-C_6H_4-R] [R = H (1); CH_3 (2); OMe (3); CF_3 (4); Cl (5); Br (6)] with $Mo(CO)_6$ in THF

The reactions of ligand precursors [C_5H_4N-2-C(H)=N-C_6H_4-R] [R = H (**1**); CH_3 (**2**); OMe

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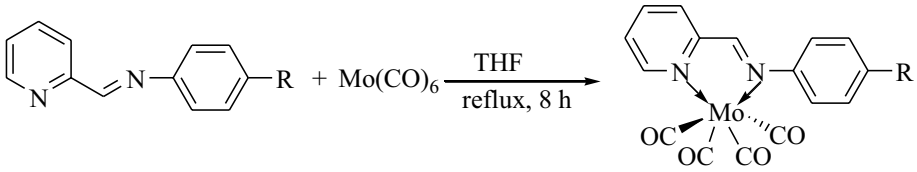
Scheme 1 Synthesis of the complexes **7**–**12**



R=H (**7**), CH_3 (**8**), OMe (**9**), CF_3 (**10**), Cl (**11**), Br (**12**)

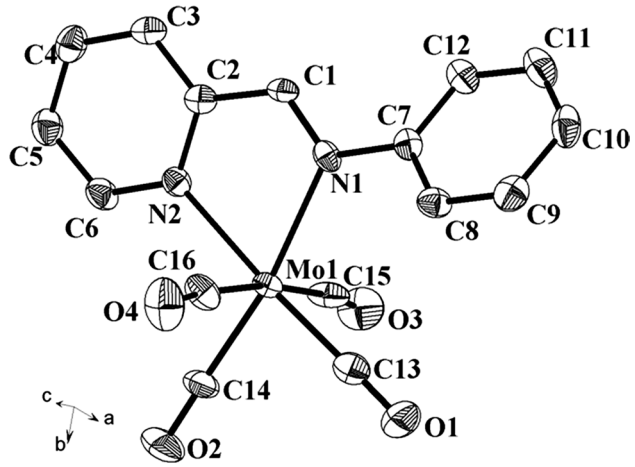


Fig. 1 ORTEP diagram of **7**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity

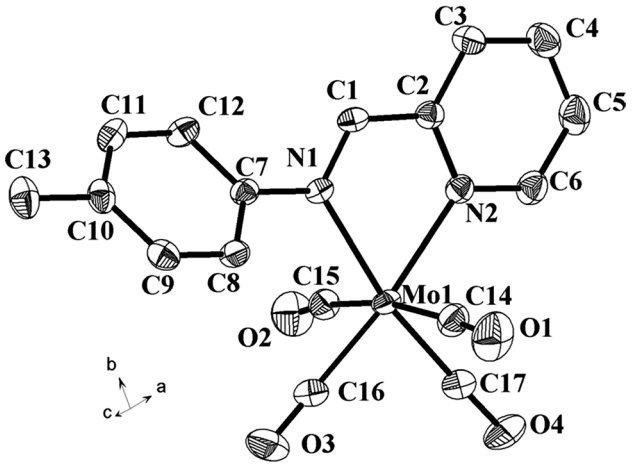


Fig. 2 ORTEP diagram of **8**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity

(**3**); CF_3 (**4**); Cl (**5**); Br (**6**)] with $Mo(CO)_6$ in refluxing THF gave the corresponding mononuclear tetracarbonyl molybdenum complexes [(η^2-2-C_5H_4N)CH=N(C_6H_4-4-R)] $Mo(CO)_4$ [R = H (**7**); CH_3 (**8**); OMe (**9**); CF_3 (**10**); Cl (**11**); Br (**12**)] (Scheme 1).

The IR spectra of **7**–**12** all exhibited three strong terminal carbonyl absorptions at 2012, 1885 and 1815 cm^{-1}. The ^1H NMR spectra of the molybdenum complexes **7**–**12** are similar, and they all show four groups of peaks at 7.82–9.21 ppm for the pyridyl protons and two doublets at 6.99–7.76 ppm for phenyl protons. The molecular structures of **7**, **8** and **10** are presented in Figs. 1, 2 and 3, respectively. These complexes are mononuclear molybdenum tetracarbonyl complexes, crystal system triclinic, space group $P\bar{1}$. The bidentate iminopyridine ligands bind to the metal center to form five-membered metallacycles. In the tetracarbonyl molybdenum complexes, the metal center occupies a distorted octahedral environment with distortions imposed by the 1,2-diimine ligand. These complexes have slightly distorted octahedral geometry with a facial arrangement of the three carbonyl groups around the Mo center. The N1–Mo–N2 bite angles are $72.9(2)^0$ for

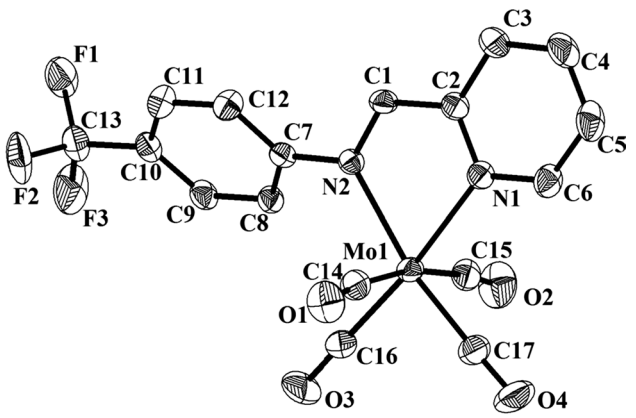
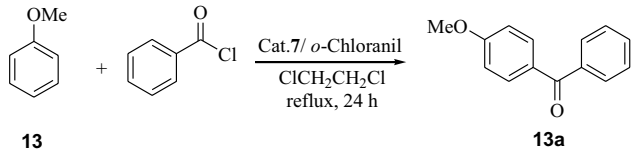


Fig. 3 ORTEP diagram of 1**0**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity

7, $72.52(9)^0$ for **8** and $72.10(14)^0$ for **10**, in correspondence to previously reported molybdenum complexes with pyridine-derived 1,2-diimine ligands. All bond lengths and angles are comparable with typical values reported for structurally similar complexes [26].



Scheme 2 Catalyzed Friedel–Crafts acylation reaction of anisole with benzoyl chloride

Table 1 Optimization of the complex (**7**)/*o*-chloranil-catalyzed reaction

Entry	*T* (°C)	Cat. **7**	*o*-chloranil (mol%)	*T* (h)	Yield (%)
1	80	0	120	24	–
2	80	20	0	24	–
3	80	20	80	12	6.2
				24	12.3
4	80	20	120	12	9.3
				24	18.2
5	80	20	160	12	10.9
				24	18.6
6	80	10	60	12	3.2
				24	5.6
7	80	15	90	12	6.2
				24	9.9
8	80	20	120	12	9.3
				24	18.2
9	80	25	150	12	11.2
				24	19.0

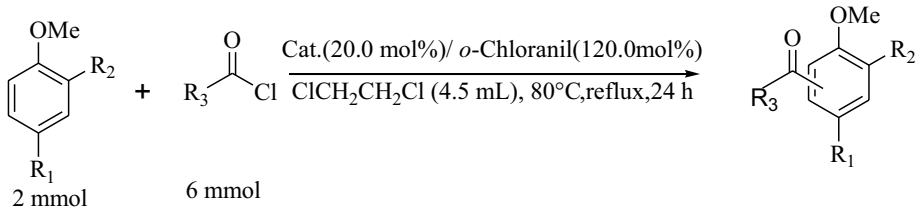
Catalytic studies

To develop an optimal catalytic system, we first investigated complex **7** as a precatalyst on the Friedel–Crafts reaction of anisole and benzoyl chloride (Scheme 2, Table 1). A solution of anisole (2 mmol) and benzoyl chloride (6 mmol) in 1,2-dichloroethane (4.5 mL) was refluxed in the presence of a catalytic amount of the precatalyst (20 mol%) and different amounts of *o*-chloranil under an argon atmosphere. By refluxing in 1,2-dichloroethane, *para*-substituted product was obtained. The conversion rate reached to 18.2% for *para* selectivity in 24 h (Table 1, entry 4). When the experiment was carried out under the absence of complex **7** or *o*-chloranil, all the results showed that no products were obtained (Table 1, entry 1 and 2), which suggested that an electrophilic substitution mechanism was involved in the complex **7**/*o*-chloranil.

In order to test the capability of Friedel–Crafts acylation reactions (Scheme 3) catalyzed by these mononuclear tetracarbonyl molybdenum complexes, influencing factors such as the reaction time, yield, economic considerations were considered. The optimized experimental conditions were as follows: 1,2-dichloroethane as solvent; the molar ratio 1:3 of aromatic substrates and acylation reagents; the amount of catalyst was 20 mol% (substrate as reference); the molar ratio of catalyst to oxidant was 1:6; reflux temperature; reaction time 24 h.

All six of molybdenum complexes proved to be capable of catalyzing Friedel–Crafts acylation reactions. The yields were found to vary with the different catalysts, and the catalytic results for complexes **7**–**12** are shown in Table 2. Friedel–Crafts-type reactions are electrophilic substitution reactions; however, the halogen and carbonyl can undergo p-π conjugation in the acylating agent, making the acylating agents more reluctant to lose halogen element to form a carbocation. Cyclohexyl chloride and cinnamyl chloride were used as acylation reagents in these reactions, and the corresponding acyl products were obtained with high selectivity for the *para*-products without detection of *di*-substituted in all cases, suggesting that the catalytic reaction has high regioselectivity. The order of increasing reactivity was found to be: 4-methyl anisole < 2-bromoanisole < 2-methylanisole < anisole, which was consistent with the characteristics of the aromatic electrophilic substitution mechanism. Overall, all six complexes gave similar results, showing that the different ligands have only a small influence on the catalytic behavior.

Scheme 3 Catalyzed Friedel–Crafts acylation reactions of benzene derivatives with acyl chlorides

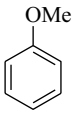
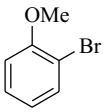
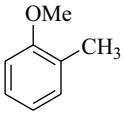
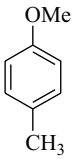


R_2= H; R_1= H (**13**), CH_3 (**14**)

R_1= H; R_2= Br (**15**), CH_3 (**16**)

R_3 = Ph (**a**), $PhCH_2$ (**b**), PhCH= CH (**c**), *c*-C_6H_{11} (**d**)

Table 2 Catalyzed Friedel–Crafts acylation reaction of aromatic substrates with different acylation reagents

Entry	Benzene derivatives	Reagents	Yield (%) catalyzed by **7**	Yield (%) catalyzed by **8**	Yield (%) catalyzed by **9**	Yield (%) catalyzed by **10**	Yield (%) catalyzed by **11**	Yield (%) catalyzed by **12**
1		PhCOCl	18.2	18.6	16.5	12.1	20.1	19.7
2		$PhCH_2COCl$	13.3	12.6	12.5	4.5	11.4	12.3
3		PhCH=CHCOCl	34.7	46.0	29.5	20.7	27.6	30.2
4		*c*-$C_6H_{11}COCl$	52.4	63.1	45.3	42.1	45.3	47.2
5		PhCOCl	12.3	5.3	9.6	5.5	10.5	11.3
6		$PhCH_2COCl$	7.3	4.2	5.4	2.7	6.3	5.6
7		PhCH=CHCOCl	21.3	22.3	14.5	13.0	16.1	18.2
8		*c*-$C_6H_{11}COCl$	35.5	30.8	19.1	21.1	20.1	20.7
9		PhCOCl	16.5	12.2	17.2	11.2	19.2	16.2
10		$PhCH_2COCl$	11.2	7.2	14.3	6.3	12.3	11.3
11		PhCH=CHCOCl	30.7	42.7	32.3	21.2	30.2	32.2
12		*c*-$C_6H_{11}COCl$	47.2	57.9	50.2	37.2	50.3	42.2
13		PhCOCl	12.3	9.3	9.3	10.2	10.9	11.2
14		$PhCH_2COCl$	7.5	5.2	7.2	3.2	7.3	7.3
15		PhCH=CHCOCl	21.2	20.1	18.2	14.2	20.3	21.5
16		*c*-$C_6H_{11}COCl$	30.2	32.3	27.2	27.2	30.2	27.2

Reagents and conditions: molar ratio: benzene derivatives/reagent = 1:3; catalyst/*o*-chloranil = 1:6, solvent: 1,2-dichloroethane 4.5 mL, 80 °C, 24 h, – = not detected

Conclusions

A series of molybdenum carbonyl complexes was prepared by reaction of pyridine imines [C_5H_4N-2-C(H)=N-C_6H_4-R] [R = H (**1**), CH_3 (**2**), OMe (**3**), CF_3 (**4**), Cl (**5**), Br (**6**)] with $Mo(CO)_6$ in refluxing THF. In addition, the catalytic performance of these mononuclear molybdenum carbonyl complexes was also tested, and it was found that these complexes had obviously catalytic activity on Friedel–Crafts reactions of aromatic compounds with a variety of acylation reagents.

Experimental

General considerations

Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive complexes. All solvents were distilled from appropriate drying agents under an atmosphere of nitrogen prior to use. Ligand precursors [C_5H_4N-2-C(H)=N-C_6H_4-R] [R = H (**1**); CH_3 (**2**); OMe (**3**); CF_3 (**4**); Cl (**5**); Br (**6**)] were prepared according to the literature methods [27–30].

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV III-500 instrument, while IR spectra were recorded as KBr disks on a Thermo Fisher is 50 spectrometer. X-ray measurements were made on a Bruker AXS SMART 1000 CCD diffractometer with graphite monochromated Mo $K\alpha$ (λ = 0.71073 Å) radiation. Elemental analyses were performed on a Vario EL III analyzer.

Syntheses

Synthesis of 7 A solution of ligand precursor **1** (0.689 g, 3.788 mmol) and $Mo(CO)_6$ (0.300 g, 1.894 mmol) in 30 mL of THF was heated at reflux for 8 h. The solvent

was removed under reduced pressure, and the residue was placed on an Al_2O_3 column. Elution with CH_2Cl_2/petroleum ether developed a purple black band, which afforded 0.175 g (41.3%) of **7** as black crystals. Mp: 134.2 °C; Anal. Calcd for $C_{16}H_{10}N_2O_4Mo$: C, 49.25; H, 2.58; N, 7.18, Found (%): C, 49.55; H, 2.80; N, 7.43. ^{1}H NMR (ppm in DMSO, 500 MHz): δ 7.43–7.47 (*m*, 1H, C_6H_1), 7.54–7.60 (*m*, 4H, C_6H_4), 7.71–7.74 (*m*, 1H, N=C(H)), 8.21–8.26 (*m*, 2H, Py-H_2), 8.97 (*s*, 1H, Py-H), 9.05 (*d*, 1H, J = 5.5 Hz, Py-H); ^{13}C NMR (DMSO, 125 MHz): δ 122.5, 128.305, 128.9, 129.7, 130.4, 139.1, 152.2, 153.2, 154.4, 166.3, 203.9. IR(υ_{CO}, KBr, cm^{-1}): 2018(s), 1885(s), 1815(s).

Synthesis of 8 By using a procedure similar to that described above, reaction of ligand precursor **2** with $Mo(CO)_6$ gave product **8** in 41.5% yield as black crystals. Mp: 135.3 °C; Anal. Calcd for $C_{17}H_{12}N_2O_4Mo$: C, 50.51; H, 2.99; N, 6.93, Found (%): C, 50.28; H, 3.23; N, 7.15. ^{1}H NMR (ppm in DMSO, 500 MHz): δ 2.37 (*s*, 3H, CH_3), 7.34 (*d*, 2H, J = 8.0 Hz, C_6H_2), 7.48 (*d*, 2H, J = 8.5 Hz, C_6H_2), 7.68–7.71 (*m*, 1H, N=C(H)), 8.20 (*d*, 2H, J = 6.0 Hz, Py-H_2), 8.92 (*s*, 1H, Py-H), 9.02 (*d*, 1H, J = 5.5 Hz, Py-H); ^{13}C NMR (DMSO, 125 MHz): δ 121.1, 122.4, 128.2, 130.1, 130.3, 138.9, 139.1, 149.8, 153.2, 154.5, 165.4, 203.9. IR(υ_{CO}, KBr, cm^{-1}): 2013(s), 1889(s), 1811(s).

Synthesis of 9 By using a procedure similar to that described above, reaction of ligand precursor **3** with $Mo(CO)_6$ gave product **9** in 42.5% yield as black solid. Mp: 136.2 °C; Anal. Calcd for $C_{17}H_{12}N_2O_5Mo$: C, 48.59; H, 2.88; N, 6.67, Found (%): C, 49.84; H, 2.53; N, 6.89. ^{1}H NMR (ppm in $CDCl_3$, 500 MHz): δ 3.87 (*s*, 3H, OCH_3), 6.99 (*d*, 2H, J = 9.0 Hz, C_6H_2), 7.41–7.44 (*m*, 1H, N=C(H)), 7.52 (*d*, 2H, J = 9.0 Hz, C_6H_2), 7.82 (*d*, 1H, J = 8.0 Hz, Py-H), 7.90–7.93 (*m*, 1H, Py-H), 8.49 (*s*, 1H, Py-H), 9.18 (*d*, 1H, J = 5.0 Hz, Py-H); ^{13}C NMR (DMSO, 125 MHz): δ 56.1, 114.8, 123.9, 127.9, 130.1, 139.1, 145.4, 153.1, 154.6, 159.9, 164.4, 204.0. IR(υ_{CO}, KBr, cm^{-1}): 2012(s), 1880(s), 1820(s).

Synthesis of 10 By using a procedure similar to that described above, reaction of ligand precursor **4** with $Mo(CO)_6$ gave product **10** in 47.2% yield as black crystals. Mp: 140.3 °C; Anal. Calcd for $C_{17}H_9F_3N_2O_4Mo$: C, 44.56; H, 1.98; N, 6.11, Found (%): C, 44.39; H, 2.20; N, 6.34. ^{1}H NMR (ppm in $CDCl_3$, 500 MHz): δ 7.56 (*d*, 2H, J = 8.5 Hz, C_6H_2), 7.76 (*d*, 2H, J = 8.5 Hz, C_6H_2), 7.82 (*d*, 1H, J = 8.0 Hz, Py-H), 7.91 (*d*, 1H, J = 8.0 Hz, Py-H), 7.95–7.99 (*m*, 1H, N=C(H)), 8.57 (*s*, 1H, Py-H), 9.21 (*d*, 1H, J = 5.0 Hz, Py-H); ^{13}C NMR (DMSO, 125 MHz): δ 123.4, 124.3, 127.05, 127.1, 128.7, 129.7, 130.9, 139.2, 153.3, 154.2, 168.1, 203.7. IR(υ_{CO}, KBr, cm^{-1}): 2010(s), 1885 (s), 1815(s).

Synthesis of 11 By using a procedure similar to that described above, reaction of ligand precursor **5** with $Mo(CO)_6$ gave product **11** in 40.1% yield as black solid. Mp: 137.5 °C; Anal. Calcd for $C_{16}H_9ClN_2O_4Mo$: C, 45.25; H, 2.14; N, 6.60, Found (%): C, 45.52; H, 2.35; N, 6.38. ^{1}H NMR (ppm in DMSO, 500 MHz): δ 7.61–7.66 (*m*, 4H, C_6H_4), 7.73–7.76 (*m*, 1H, N=C(H)), 8.24 (*q*, 2H, J = 6.0 Hz, Py-H), 8.98 (*s*, 1H, Py-H), 9.06 (*d*, 1H, J = 5.0 Hz, Py-H); ^{13}C NMR (DMSO, 125 MHz): δ 124.3, 128.4, 129.7, 130.6, 133.1, 139.1, 150.9, 153.3, 154.3, 166.9, 203.8. IR(υ_{CO}, KBr, cm^{-1}): 2013(s), 1886(s), 1816(s).

Synthesis of 12 By using a procedure similar to that described above, reaction of ligand precursor **6** with $Mo(CO)_6$ gave product **12** in 42.3% yield as black solid. Mp: 138.3 °C; Anal. Calc. for $C_{16}H_9BrN_2O_4Mo$: C, 40.97; H, 1.93; N, 5.97, Found (%): C, 41.22; H, 1.68; N, 6.25. ^{1}H NMR (ppm in $CDCl_3$, 500 MHz): δ 7.38 (*d*, 2H, J = 8.5 Hz, C_6H_2), 7.46–7.49 (*m*, 1H, N=C(H)), 7.61 (*d*, 2H, J = 8.5 Hz, C_6H_2), 7.87 (*d*, 1H, J = 7.5 Hz, Py-H), 7.93–7.96 (*m*, 1H, Py-H), 8.57 (*s*, 1H, Py-H), 9.20 (*d*, 1H, J = 5.5 Hz, Py-H); ^{13}C NMR (DMSO, 125 MHz): δ 124.3, 128.5, 129.7, 130.6, 133.1, 139.2, 150.9, 153.3, 154.3, 166.9, 203.8. IR(υ_{CO}, KBr, cm^{-1}): 2013(s), 1887(s), 1813(s).

Crystal structure determination

Crystals of complexes **7**, **8** and **10** suitable for X-ray diffraction were investigated with a Bruker AXS SMART 1000 CCD diffractometer, using graphite monochromated Mo $K\alpha$ radiation (φ/ω scan, λ = 0.71073 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 [31]. Crystallographic data and experimental details of the structure determinations are given in Table 3. Selected bond lengths and angles are given in Table 4.

General procedure for catalytic tests

The catalytic reactions were carried out under an argon atmosphere with magnetic stirring. The required Mo complex (0.4 mmol) and *o*-chloranil (0.57 g, 2.4 mmol) was mixed with 1,2-dichloroethane (4.5 mL) in a 25-mL round-bottom flask at room temperature. Aromatic compounds (2 mmol) and acylation reagents (2 mmol) were added by syringe. The reaction mixture was heated at 80 °C for 24 h. After cooling to room temperature, the solid catalyst was separated from the reaction mixture by filtration. The solvent was removed by rotary evaporation, and the residue was purified by Al_2O_3 column chromatography, eluting with petroleum ether and dichloromethane to give the

Table 3 Crystal data and structure refinement parameters for **7**, **8** and **10**

Complex	**7**	**8**	**10**
Empirical formula	$C_{16}H_{10}N_2O_4Mo$	$C_{17}H_{12}N_2O_4Mo$	$C_{17}H_9F_3MoN_2O_4$
Formula weight	390.20	404.23	458.2
Temperature (K)	298 (2)	298 (2)	298 (2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.3460 (7)	7.3860 (7)	8.1010 (8)
b (Å)	9.1439 (9)	9.0689 (9)	9.0349 (9)
c (Å)	12.3961 (11)	13.3361 (12)	13.2401 (12)
α (°)	84.506 (2)	80.100 (2)	79.751 (2)
β (°)	78.3090 (10)	77.0520 (10)	77.899 (2)
γ (°)	70.4220 (10)	70.7550 (10)	69.2510 (10)
V (Å^3)	767.90 (13)	817.25 (13)	880.36 (15)
Z	2	2	2
F (000)	388	404	452
Dcalc (g/cm^3)	1.688	1.643	1.729
Crystal dimensions (mm)	0.45 × 0.37 × 0.25	0.49 × 0.48 × 0.45	0.45 × 0.40 × 0.04
θ Range (°)	2.37–25.02	2.72–25.02	2.43–25.01
Reflections collected	3774	4142	4484
Independent reflections	2629	2836	3055
R_{int}	0.0248	0.0219	0.039
Parameters	208	336	272
Goodness of fit on F^2	1.271	1.052	1.083
R_1, wR_2 [$I > 2\sigma(I)$]	0.0589, 0.1524	0.0311, 0.0822	0.0589, 0.1524
R_1, wR_2 (all data)	0.0657, 0.1544	0.0347, 0.0850	0.0657, 0.1544
CCDC deposition no.	1492231	1487562	1509950

Table 4 Selected bond distances (nm) and angles (°) for **7**, **8** and **10**

7		**8**		**10**	
Mo(1)-N(2)	2.242 (7)	Mo(1)-N(2)	2.235 (3)	Mo(1)-N(1)	2.237 (4)
Mo(1)-N(1)	2.289 (7)	Mo(1)-N(1)	2.261 (2)	Mo(1)-N(2)	2.266 (4)
N(1)-C(1)	1.276 (10)	N(1)-C(1)	1.285 (4)	N(2)-C(1)	1.282 (6)
N(2)-C(2)	1.368 (10)	N(2)-C(2)	1.350 (4)	N(1)-C(2)	1.341 (6)
C(1)-C(2)	1.441 (11)	C(1)-C(2)	1.441 (4)	C(1)-C(2)	1.443 (7)
N(2)-Mo(1)-N(1)	72.9 (2)	N(2)-Mo(1)-N(1)	72.52 (9)	N(1)-Mo(1)-N(2)	72.10 (14)
C(1)-N(1)-Mo(1)	114.6 (5)	C(1)-N(1)-Mo(1)	115.62 (19)	C(1)-N(2)-Mo(1)	116.0 (3)
C(2)-N(2)-Mo(1)	116.0 (5)	C(2)-N(2)-Mo(1)	116.73 (19)	C(2)-N(1)-Mo(1)	117.0 (3)
O(1)-C(13)-Mo(1)	178.5 (8)	O(1)-C(14)-Mo(1)	174.0 (4)	O(1)-C(14)-Mo(1)	172.4 (5)
O(3)-C(15)-Mo(1)	173.3 (8)	O(3)-C(16)-Mo(1)	179.4 (3)	O(3)-C(16)-Mo(1)	179.9 (7)

corresponding products. The progress of the reaction was monitored using an Agilent 6820 gas chromatograph.

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