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Synthesis of (η^6-arene)tricarbonylmetal and (σ-nitrogen)pentacarbonylmetal complexes of 1,2,3,4-tetrahydroquinoline and 1,2,3,4-tetrahydroisoquinoline with chromium, molybdenum and tungsten

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Abstract

Thermal reactions of [M(CO)$_6$] with 1,2,3,4-tetrahydroquinoline (**1**) afford the corresponding (η^6-arene)tricarbonylmetal complex (M = Cr, **3**; M = Mo, **4**; and M = W, **5**). In contrast, thermolysis of the same hexacarbonyl complexes with 1,2,3,4-tetrahydroisoquinoline (**2**) affords the (σ-nitrogen)pentacarbonylmetal derivatives (M = Cr, **7**; M = Mo, **8**; and M = W, **9**). For chromium the (η^6-arene)tricarbonylmetal complex (**6**) was also isolated. X-ray crystal structures are reported for **3**, **4**, **7** and **9**.

Keywords: Arene; Tetrahydroquinoline; Tetrahydroisoquinoline; Chromium; Molybdenum; Tungsten

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1. Introduction

Among the most important processes in the treatment of petroleum, are those denominated as hydrotreating, i.e. hydrodesulfurization, hydrodeoxygenation, hydrodenitrogenation and hydrodemetallation. These processes are used to reduce the presence of several contaminants such as sulfur, oxygen, nitrogen and metalloporphyrins. The importance of the elimination of these components is that they not only poison catalysts used in refining processes but also, if present in fuels, pollutants as sulfur and nitrogen oxides (SO$_2$, NO$_x$) produced during the combustion are released to the atmosphere. Therefore, increased research efforts have been made to reduce these pollutant emissions [1]. In the case of nitrogen, this exists in crude oil as aromatic heterocycles, aliphatic and aromatic amines and nitriles. Among these the aromatic heterocycles (e.g. quinoline and isoquinoline) are the most difficult to treat [2]. Since removal of nitrogen from these compounds requires hydrogenation of at least the heterocyclic ring, compounds **1** and **2** can be considered as possible intermediates in HDN reactions [3]. Thus, the study of the reactivity of heterocyclic species towards metal fragments in order to establish the bonding modes of such compounds to metal centers becomes very important with respect to HDN chemistry.

Recent reviews in the area [4] have established that nitrogen containing ligands can coordinate to metal fragments in different fashions; for example, as η^1(N), η^6(π C) and η^2(N = C). The η^1(N) complexes are obtained when a lone-pair in the heteroatom is available [4–6] or when a product of N–H bond activation is isolated; regarding the latter example our group has reported examples on this kind of reactivity [7]. There are several examples for the η^6(π C) coordination mode with metal carbonyls and nitrogen based ligands [8–10].

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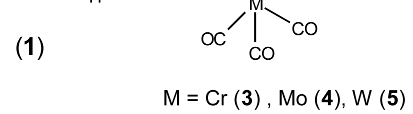
The methods for preparing these compounds vary from reactions in ether like solvents at elevated temperatures and/or the use of UV light to assist CO removal [10], to synthesis using reagents able to transfer the tricarbonyl moiety to aromatic systems under relatively mild conditions [11]. Among the complexes containing the carbonylchromium moiety, the arene derivatives of aniline and *N*-methyl analogues [12], mono-, di and tri-benzylpyrroles [13], 1-aminonaftalene [14], cyclic amines and their *N*-aliphatic analogues [15], and several *N*-heteroaromatic compounds (indole, carbazole, benzoacridine, benzoquinolines, phenyl and silylpyridines and quinaldine) [11,16] have been reported. In contrast to chromium, analogous examples with the carbonylmolybdenum and carbonyltungsten moieties [17] are less common.

Here we wish to report the preparation of η^1(N) compounds and η^6-arenes containing hydrogenated heterocyclic rings, species which may be possible intermediates in the HDN reaction.

2. Results and discussion

The thermolysis of [M(CO)$_6$] (M = Cr, Mo or W) with **1** affords the corresponding (η^6-arene)tricarbonylmetal complexes **3**–**5** (Scheme 1). As expected, the ^{1}H-NMR spectra of the compounds display aromatic protons that are shifted to high field, ca. 2 ppm in comparison with the free ligand [18]. In contrast, the chemical shifts of the aliphatic protons do not change significantly; however, there is a clear differentiation of the protons in the equatorial and axial positions due to coordination to the [M(CO)$_3$] moiety. Moreover, the ^{13}C-NMR spectra confirm the loss of aromatic character in the benzene ring with chemical shifts for these carbons located in the range of δ 77–136; a shift of about 30 ppm to high field with respect to the free ligand [19]. The aliphatic carbons, however, are virtually unaffected by the complexation as has been observed previously in similar complexes [20]. In all cases signals corresponding to the carbonyl ligands are located at 236 ppm. Compounds **3**–**5** each show two strong bands (A_1+E) for the carbonyl ligands in the IR spectra in agreement with the local C_{3v} symmetry [21]. In complex **3**, for instance, these absorptions are located at 1954 and 1874 cm^{-1}.



Scheme 1.

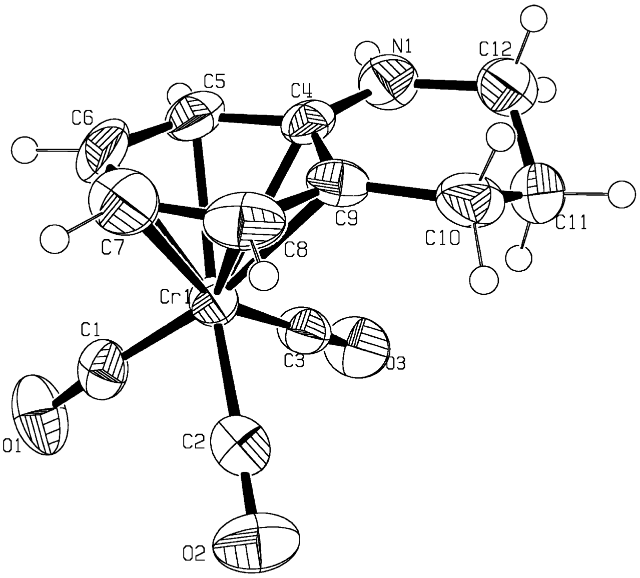


Fig. 1. Molecular structure of complex **3** with thermal ellipsoids at the 50% level.

The molecular structures of complexes **3** and **4** were confirmed by single crystal X-ray diffraction experiments (Figs. 1 and 2 and Tables 1 and 2, respectively). Both complexes exhibit typical three-legged piano stool geometry and selected bond lengths and angles are given in Tables 1 and 2. The compounds are essentially isostructural with the metal center (chromium or molybdenum) bound equally to all of the aromatic carbons [22]. The C–C double bond distances and bond angles of the aromatic system all fall within the expected values [23].

Ligand **2** reacts with [Cr(CO)$_6$] to yield a mixture of two complexes: the η^6 arene type complex **6**, and the σ-

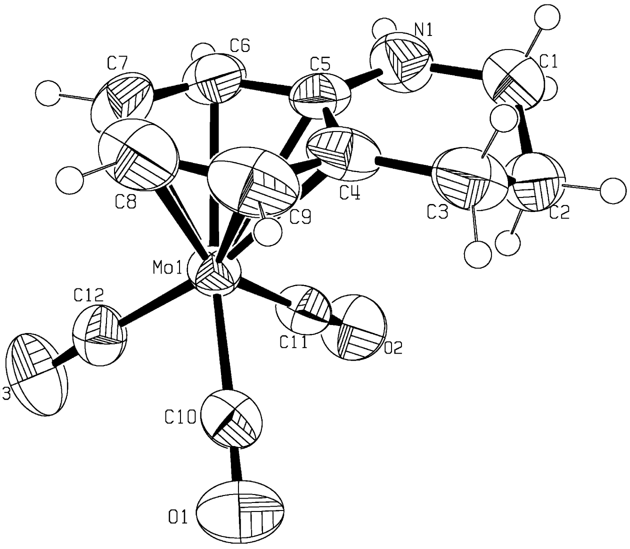


Fig. 2. Molecular structure of complex **4** with thermal ellipsoids at the 50% level.

Table 1
Selected bond lengths (Å) and bond angles (°) for **3**

Bond lengths			
Cr(1)–C(4)	2.368(6)	Cr(1)–C(8)	2.189(6)
Cr(1)–C(5)	2.243(6)	Cr(1)–C(9)	2.272(6)
Cr(1)–C(6)	2.195(6)	C(4)–N(1)	1.350(7)
Cr(1)–C(7)	2.207(6)		
Bond angles			
N(1)–C(4)–C(5)	120.0(5)		

Table 2
Selected bond lengths (Å) and bond angles (°) for **4**

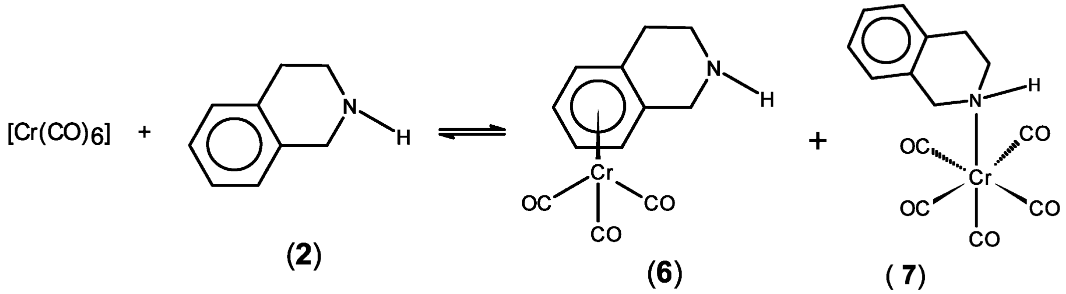
Bond lengths			
Mo(1)–C(4)	2.438(4)	Mo(1)–C(8)	2.355(5)
Mo(1)–C(5)	2.511(4)	Mo(1)–C(9)	2.350(5)
Mo(1)–C(6)	2.409(4)	C(5)–N(1)	1.363(5)
Mo(1)–C(7)	2.351(5)		
Bond angles			
N(1)–C(5)–C(6)	119.4(4)		

N bonded derivative **7** (Scheme 2). The ^{1}H-NMR spectrum for complex 6 shows the shifting of the aromatic protons and carbons to high field (ca. 2 ppm for ^{1}H and 28 ppm for ^{13}C) and the aliphatic protons again become inequivalent. In contrast, reaction of **2** with [Mo(CO)$_6$] or [W(CO)$_6$] under similar conditions generates only the mono σ-N bonded derivatives **8** and **9**, respectively (Scheme 3). The ^{1}H-NMR spectra of **7**, **8** and **9** show virtually no change in the chemical shift of the aromatic protons in comparison with the free ligand; but the aliphatic protons become chemically and magnetically inequivalent. Moreover, in the ^{13}C-NMR spectra of **7**, **8** and **9** two important features can be observed; first, the aromaticity of the benzene protons remains unaltered and second, the existence of two types of carbonyl ligands is evident. Also, a dynamic ring inversion process can be observed in the ^{13}C-NMR spectra of **8** and **9** as both complexes exhibit six signals for the aliphatic moiety at room temperature. Similar behavior has been observed previously in related compounds [24]. Upon warming solutions of **8** or **9** all signals assigned to the alkyl moiety begin broadening, eventually leading to three signals at 90 °C in the case of **8**, whereas complete coalescence could not be observed for **9** and some decomposition appeared. Cooling a solution of compound **7** results in precipitation and consequently a low-temperature limit could not be determined.

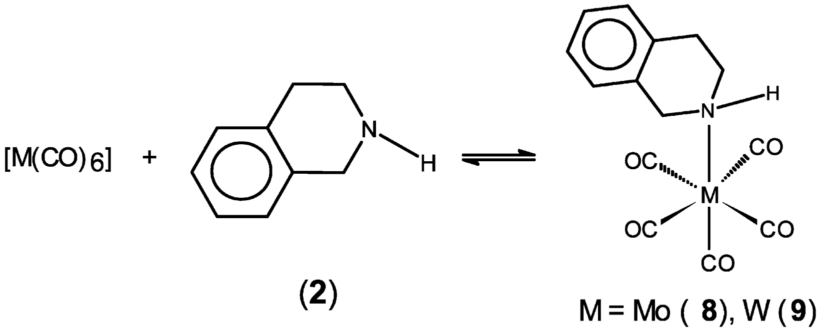
Likely associated with this dynamic process a significant disorder was observed in the aliphatic portion of the ligand for compounds **7** and **9** in the solid state via X-ray crystallographic studies (Figs. 3 and 4 and Tables 3 and 4, respectively). The disorder is depicted only for compound **9**; however, in both structures the disorder is primarily associated with the N(1)–C(3) bond. In contrast, atoms C(1) and C(4) do not present any disorder. The characteristic IR spectra for complexes of the type [M(CO)$_5$L], with a local C_{4v} symmetry is observed, constituted by three bands (2A$_1$+E) for the carbonyl ligands. For complex **7**, for instance, these absorptions are located at 2065 (s), 1933 (m) and 1900 (w) cm^{-1}.

The difference in reactivity between ligands **1** and **2** in this system is an example of the competitive formation of η^6-arene-metal bonds versus η^1-*N*-metal bonds. This difference can be explained considering the following: (a) the availability or accessibility of the unbound lone pair on the nitrogen atom in **2** [8,9a,25]; and (b) both compounds (**6** and **7**) are formed in the reaction mixture under reflux. A change in the reaction temperature, however, favors either one or the other. For instance, **6** is favored under reflux for long periods of reaction while **7** is produced in pure form by gentle warming at 90 °C. Refluxing pure **7** in heptane or a solvent mixture of dioxane–heptane does not result in the formation of compound **6**. Consequently, we propose that the complexes are formed via independent pathways. It is noteworthy that similarly to **7**, complexes **8** and **9** do not lead to the formation of the corresponding η^6-arene complexes.

Finally, the molybdenum compounds are formed faster but among the triad are the least stable [26]. It was also observed that the η^1-N complexes decompose thermally, regenerating the free ligand and [M(CO)$_6$] and other decomposition products as previously observed in similar systems [27].



Scheme 2.



Scheme 3.

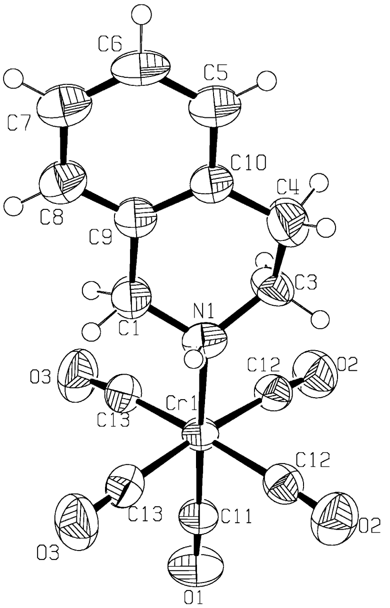


Fig. 3. Molecular structure of complex **7** with thermal ellipsoids at the 50% level.

3. Conclusions

It was demonstrated that the direct interaction of hexacarbonyl–metals of Group 6 with **1** generates in all cases the η^6-arene type complexes. While the reaction with **2** affords mainly the η^1-N bonded compounds; only in the case of chromium were both type of compounds isolated.

Work aimed to explore the reactivity of the complexes reported here with a variety of nucleophiles, including the attack by a second electron rich metal center is currently under process.

4. Experimental

All reactions and purifications were carried out under argon atmosphere using vacuum line, Schlenk tube and drybox techniques. Solvents were dried and distilled

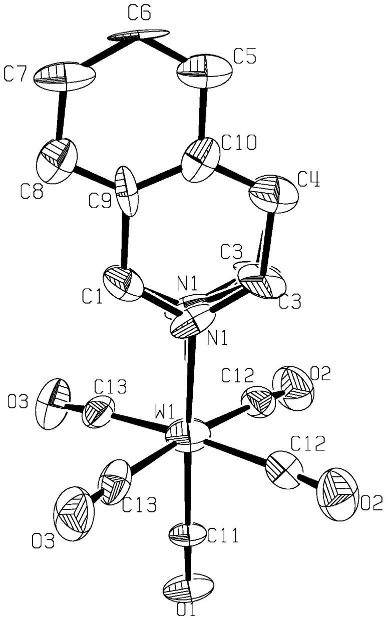


Fig. 4. Molecular structure of complex **9** with thermal ellipsoids at the 50% level. H atoms omitted for clarity, with a disorder depicted at C3 and N1.

Table 3
Selected bond lengths (Å) and bond angles (°) for **7**

Bond lengths			
Cr(1)–N(1)	2.222(7)	Cr(1)–C(12)	1.906(5)
Cr(1)–C(11)	1.837(6)	Cr(1)–C(13)	1.898(5)
Bond angles			
C(13)–Cr(1)–C(12)	90.18(19)		

Table 4
Selected bond lengths (Å) and bond angles (°) for **9**

Bond lengths			
W(1)–N(1)	2.33(2)	W(1)–C(12)	2.050(16)
W(1)–C(11)	1.974(19)	W(1)–C(13)	2.041(17)
Bond angles			
C(13)–W(1)–C(12)	91.6(6)		

before use. Deuterated solvents (Cambridge Isotope) for NMR experiments were dried over molecular sieves. 1,2,3,4-tetrahydroquinoline and 1,2,3,4-tetrahydroisoquinoline were distilled under reduced pressure, stored under argon and dried over molecular sieves. All other chemicals were reagent grade and used as received. ^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded on a Varian VXR-300 spectrometer in 1,4-dioxane-d^{8}, unless otherwise stated; chemical shifts (δ) are related to deuterated solvent. Infrared spectra were obtained on a Perkin–Elmer 1600 FT spectrophotometer and mass determinations (LR and HR) on a JEOL SX-102 A, using EI as ionization technique. Elemental analyses were done in an EAGER 200 for the most stable compounds and high resolution mass spectroscopy for the most unstable ones.

4.1. Preparation of tricarbonyl[η^{6}-1,2,3,4-tetrahydroquinoline]chromium (**3**)

A mixture of 1,2,3,4-tetrahydroquinoline (0.25 ml, 1.95 mmol) and hexacarbonylchromium (0.65 g, 2.93 mmol) was heated to reflux in 10 ml of 1,4-dioxane under argon atmosphere until a greenish brown precipitate appeared (38 h). The solution was then allowed to cool and then filtered through Celite. The solvent was removed in vacuo (20 °C/0.2 mmHg); the remaining yellow oil was washed with hexanes at room temperature (r.t.). The complex was crystallized from ether–hexane. Pure compound yield: 53%. Anal. Calc. for $C_{12}H_{11}NCrO_3$: C, 53.54; H, 4.12. Found: C, 52.99; H, 4.19%. IR in ether: ν(C–O) 1954 and 1874 cm^{-1}. m/z: 269 [M^{+}]. NMR spectra are as follows, ^{1}H: δ 1.86 (m, CH$_2$, 1H); 1.94 (m, CH$_2$, 1H), 2.52 (m, CH$_2$, 2H), 3.05 (m, CH$_2$, 1H), 3.28 (m, CH$_2$, 1H), 4.80 (d, CH, 1H, $^{3}J_{HH} = 6.89$ Hz), 4.86 (t, CH, 1H, $^{3}J_{HH} = 6.29$ Hz), 5.24 (s, NH, 1H), 5.50 (t, CH, 1H, $^{3}J_{HH} = 6.60$ Hz), 5.64 (d, CH, 1H, $^{3}J_{HH} = 6.29$). ^{13}C{^{1}H}: δ 21.92 (s, CH$_2$), 26.80 (s, CH$_2$), 41.46 (s, CH$_2$), 77.04 (s, CH), 83.36 (s, CH), 91.57 (s, C), 97.15 (s, CH), 99.50 (s, CH), 132.78 (s, C) and 236.45 (s, CO).

4.2. Preparation of tricarbonyl[η^{6}-1,2,3,4-tetrahydroquinoline]molybdenum (**4**)

A mixture of 1,2,3,4-tetrahydroquinoline (0.19 ml, 1.48 mmol) and hexacarbonylmolybdenum (0.61 g, 2.26 mmol) was heated to reflux in a mixture of 1,4-dioxane–heptane (15:7) under an argon atmosphere until a dark brown precipitate appeared (40 h). The solution was then allowed to cool and filtered through Celite. The solvent was removed in vacuum (20 °C/0.2 mmHg); the remaining yellow oil was washed with hexanes and the yellow powder was warmed to 80 °C under vacuum and dried. Pure compound yield: 48%. HR mass: Calc. 314.9796. Found 314.9764; elemental composition $C_{12}H_{11}O_3NMo$. IR in ether: ν(C–O) 1955 and 1870 cm^{-1}. m/z: 315 [M^{+}]. NMR spectra are as follows, ^{1}H: δ 1.89 (m, CH$_2$, 2H); 2.53 (m, CH$_2$, 2H), 3.11 (m, CH$_2$, 1H), 3.24 (m, CH$_2$, 1H), 5.18 (m, CH, 2H), 5.41 (s, NH, 1H), 5.89 (t, CH, 1H, $^{3}J_{HH} = 6.59$ Hz), 6.09 (d, CH, 1H, $^{3}J_{HH} = 6.29$ Hz). ^{13}C{^{1}H}: δ 22.45 (s, CH$_2$), 27.10 (s, CH$_2$), 41.64 (s, CH$_2$), 78.85 (s, CH), 85.52 (s, CH), 95.63 (s, C), 100.31 (s, CH), 102.05 (s, CH), 136.54 (s, C) and 225.27 (s, CO).

4.3. Preparation of tricarbonyl[η^{6}-1,2,3,4-tetrahydroquinoline]tungsten (**5**)

A mixture of 1,2,3,4-tetrahydroquinoline (0.16 ml, 1.25 mmol) and hexacarbonyltungsten (0.69 g, 1.96 mmol) was heated to reflux in 15 ml of mixture of 1,4-dioxane–n-heptane (4:1) under an argon atmosphere until a dark brown precipitate appeared (36 h). The solution was allowed to cool, filtered through Celite and the solvent was removed in vacuo (20 °C/0.2 mmHg); a yellow powder was obtained. The residue was then washed with hexanes at r.t. and the remaining solid was warmed to 80 °C under vacuum. The complex was isolated as a yellow powder. Pure compound yield: 37%. HR mass: Calc. 401.0250. Found 401.0284; elemental composition $C_{12}H_{11}O_3NW$. IR in ether: ν(C–O) 1952 and 1868 cm^{-1}. m/z: 401 [M^{+}]. NMR spectra are as follows, ^{1}H: δ 1.86 (m, CH$_2$, 2H); 2.56 (m, CH$_2$, 2H), 3.19 (m, CH$_2$, 1H), 3.29 (m, CH$_2$, 1H), 5.11 (td, CH, 2H, $^{3}J_{HH} = 5.40$; $^{4}J_{HH} = 1.20$), 5.40 (s, NH, 1H), 5.70 (td, CH, 1H, $^{3}J_{HH} = 6.44$ Hz; $^{4}J_{HH} = 1.20$ Hz), 5.90 (d, CH, 1H, $^{3}J_{HH} = 5.99$ Hz). ^{13}C{^{1}H}: δ 22.28 (s, CH$_2$), 27.19 (s, CH$_2$), 41.52 (s, CH$_2$), 74.04 (s, CH), 82.66 (s, CH), 91.43 (s, C), 95.84 (s, CH), 97.36 (s, CH), 134.33 (s, C) and 214.72 (s, CO).

4.4. Preparation of tricarbonyl[η^{6}-1,2,3,4-tetrahydroisoquinoline]chromium (**6**) and pentacarbonyl[η^{1}-1,2,3,4-tetrahidroisoquinoline]chromium (**7**)

A mixture of 1,2,3,4-tetrahydroisoquinoline (0.30 ml, 2.30 mmol) and hexacarbonylchromium (1.53 g, 6.90 mmol) was heated to reflux in 15 ml of 1,4-dioxane and 2 ml of heptane under an argon atmosphere until a greenish brown precipitate appeared (40 h). The solution was allowed to cool and filtered through Celite. The solvent was removed in vacuum (20 °C/0.2 mmHg); the remaining orange oil was washed with ether at r.t. The filtrate is rich in **7**; the solvent was evaporated and the complex was crystallized from acetone and hexane. Heptane was added to the residue, i.e. to the solid non-soluble in ether and was refluxed for 24 h; the solvent was removed and the remaining solid was washed with hexane at −10 °C to yield **6**.

Complex **7** can also be prepared in high purity if instead of refluxing conditions the mixture is gently warmed at 90 °C for 12 h.

6: yield, 31%. Anal. Calc. for $C_{12}H_{11}NCrO_3$: C, 53.54; H, 4.12. Found: C, 51.54; H, 4.42%. HR mass: Calc. 269.0144. Found 269.0157; elemental composition $C_{12}H_{11}O_3NCr$. IR in ether: ν(C–O) 1969 and 1889 cm^{-1}. *m/z*: 269 [M^+]. NMR spectra are as follows. ^1H: δ 1.83 (s, NH, 1H); 2.54 (m, CH_2, 2H), 2.95 (m, CH_2, 2H), 3.74 (m, CH_2, 2H), 5.37 (m, CH, 4H). $^{13}C\{^1H\}$: δ 28.77 (s, CH_2), 43.31 (s, CH_2), 47.60 (s, CH_2), 92.65 (s, CH), 92.91 (s, CH), 93.26 (s, CH), 94.98 (s, CH), 109.48 (s, C), 111.12 (s, C) and 234.73 (s, CO).

7: yield, 10%. Anal. Calc. for $C_{14}H_{11}NCrO_5$: C, 51.69; H, 3.38. Found: C, 50.48; H, 3.30%. HR mass: Calc. 325.0042. Found 325.0074; elemental composition $C_{14}H_{11}O_5NCr$. IR in ether: ν(C–O) 2065, 1933 and 1900 cm^{-1}. *m/z*: 325 [M^+]. NMR spectra are as follows. ^1H: δ 2.69 (m, CH_2, 1H); 2.84 (m, CH_2, 1H), 3.04 (m, CH_2, 1H), 3.28 (m, CH_2, 1H), 3.64 (s, NH, 1H), 3.94 (m, CH_2, 2H), 7.10 (m, CH, 4H). $^{13}C\{^1H\}$: δ 29.49 (s, CH_2), 55.23 (s, CH_2), 59.32 (s, CH_2), 126.54 (s, CH), 126.94 (s, CH), 127.73 (s, CH), 129.48 (s, CH), 133.30 (s, C), 135.61 (s, C), 215.28 (s, CO) and 220.42 (s, CO).

*4.5. Preparation of pentacarbonyl[η-1,2,3,4-tetrahydroisoquinoline]molybdenum (**8**)*

A mixture of 1,2,3,4-tetrahydroisoquinoline (0.16 ml, 1.23 mmol) and hexacarbonylmolybdenum (1 g, 3.71 mmol) was heated to reflux in 15 ml of 1,4-dioxane and 5 ml of heptane under an argon atmosphere until a dark brown precipitate appeared (20 h). The solution was then allowed to cool and filtered through Celite. The solvent was removed in vacuo (20 °C/0.2 mmHg); the remaining oil was washed with hexanes and the yellow powder was dried. Pure compound yield: 54%. HR mass: Calc. 370.9694. Found 370.9721; elemental composition $C_{14}H_{11}O_5NMo$. IR in ether: ν(C–O) 2071,

Table 5
Summary of crystallographic results of **3**, **4**, **7** and **9**

Complexes	**3**	**4**	**7**	**9**
Empirical formula	$C_{12}H_{11}CrNO_3$	$C_{12}H_{11}MoNO_3$	C_{14} H_{11} Cr N O_5	C_{14} H_{11} N O_5 W
Formula weight	268.21	313.16	325.24	457.09
Temperature	293(2) K	298(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 A	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*	*Pnma*	*Pnma*
Unit cell dimensions				
a (Å)	12.386(6)	12.4326(13)	13.824(1)	14.006(2)
b (Å)	12.423(6)	12.6218(13)	7.974(1)	8.003(1)
c (Å)	14.693(7)	15.1165(15)	12.665(1)	12.792(2)
α (°)	90	90	90	90
β (°)	90	90	90	90
γ (°)	90	90	90	90
V ($Å^3$)	2260.8(18)	2372.1(4)	1396.1(2)	1433.9(4)
Z	8	8	4	4
D_{calc} (Mg m^{-3})	1.576	1.754	1.547	2.117
Absorption coefficient (mm^{-1})	1.005	1.100	0.839	8.076
$F(000)$	1096	1248	664	864
Crystal size (mm^3)	0.24 × 0.15 × 0.11	0.24 × 0.14 × 0.08	0.312 × 0.090 × 0.078	0.250 × 0.024 × 0.022
θ Range for data collection (°)	2.70–22.99	2.67–26.99	2.18–24.97	2.16–25.07
Index ranges	$-13 \le h \le 13$, $-13 \le k \le 13$, $-16 \le l \le 16$	$-15 \le h \le 15$, $-13 \le k \le 16$, $-17 \le l \le 19$	$-16 \le h \le 16$, $-9 \le k \le 9$, $-15 \le l \le 14$	$-16 \le h \le 16$, $-9 \le k \le 9$, $-15 \le l \le 15$
Reflections collected	16969	11959	10850	11348
Independent reflections	1570 [$R_{int} = 0.1036$]	2582 [$R_{int} = 0.0344$]	1323 [$R_{int} = 0.0571$]	1374 [$R_{int} = 0.1088$]
Completeness to $\theta = 22.99°$ (%)	100.0	99.9	99.9	99.9
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1570/0/154	2582/0/154	1323/0/124	1374/0/121
Goodness-of-fit on F^2	1.116	0.857	1.051	0.924
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0642$, $wR_2 = 0.1297$	$R_1 = 0.0335$, $wR_2 = 0.0850$	$R_1 = 0.0706$, $wR_2 = 0.1544$	$R_1 = 0.0744$, $wR_2 = 0.1771$
R indices (all data)	$R_1 = 0.0823$, $wR_2 = 0.1376$	$R_1 = 0.0616$, $wR_2 = 0.1032$	$R_1 = 0.0889$, $wR_2 = 0.1643$	$R_1 = 0.1132$, $wR_2 = 0.1940$
Largest difference peak and hole (e $Å^{-3}$)	0.431 and −0.322	0.585 and −0.239	1.522 and −0.244	4.310 (0.81 Å from W1) and −0.677

1937and 1908 cm^{-1}. *m/z*: 371 [M$^+$]. NMR spectra are as follows: ^{1}H: δ 2.45 (s, NH, 1H); 2.75 (m, CH_2, 1H), 2.90 (m, CH_2, 1H), 3.15 (m, CH_2, 1H), 3.40 (m, CH_2, 1H), 4.05 (m, CH_2, 2H), 7.10 (m, CH, 4H). $^{13}C\{^1H\}$: δ 30.62 (s, CH_2), 30.67 (s, CH_2), 56.08 (s, CH_2), 56.22 (s, CH_2), 60.21 (s, CH_2), 60.34 (s, CH_2), 127.95 (s, CH), 128.31 (s, CH), 129.04 (s, CH), 130.87 (s, CH), 134.46 (s, C), 136.82 (s, C), 206.60 (s, CO) and 214.89 (s, CO). $^{13}C\{^1H\}$ at 90°C: δ 30.65 (s, CH_2), 56.15 (s, CH_2), 60.27 (s, CH_2), 127.95 (s, CH), 128.31 (s, CH), 129.04 (s, CH), 130.87 (s, CH), 134.46 (s, C), 136.82 (s, C), 206.60 (s, CO) and 214.89 (s, CO).

*4.6. Preparation of pentacarbonyl[η-1,2,3,4-tetrahydroisoquinoline]tungsten (**9**)*

A mixture of 1,2,3,4-tetrahydroisoquinoline (0.12 ml, 0.92 mmol) and hexacarbonyltungsten (1 g, 2.81 mmol) was heated to reflux in 15 ml of 1,4-dioxane and 5 ml of heptane under an argon atmosphere until a dark brown precipitate appeared (21 h). The solution was then allowed to cool and filtered through Celite. The solvent was removed in vacuo (20 °C/0.2 mmHg); the remaining powder was then purified by chromatography in a neutral alumina column eluting from hexane to hexane–acetone (1:1). Any unchanged starting material eluted first and the corresponding tungsten complex was isolated as a yellow powder. Pure compound yield: 50%. HR mass: Calc. 457.0149. Found 457.0115; elemental composition $C_{14}H_{11}O_5NW$. IR in ether: ν(C–O) 2069, 1929 and 1895 cm^{-1}. *m/z*: 457 [M$^+$]. NMR spectra are as follows: ^{1}H: δ 2.71 (s, CH_2, 1H); 2.92 (m, CH_2, 1H), 3.21 (m, CH_2, 1H), 3.40 (m, CH_2, 1H), 4.17 (m, CH_2, 2H), 4.46 (s, NH, 1H), 7.10 (m, CH, 4H). $^{13}C\{^1H\}$: δ 29.40 (s, CH_2), 29.96 (s, CH_2), 54.95 (s, CH_2), 56.75 (s, CH_2), 59.06 (s, CH_2), 60.82 (s, CH_2), 126.64 (s, CH), 126.68 (s, CH), 127.04 (s, CH), 127.11 (s, CH), 127.75 (s, CH), 127.88 (s, CH), 129.60 (s, CH), 132.67 (s, C), 133.18 (s, C), 135.56 (s, C), 135.89 (s, C), 205.33 (s, CO) and 213.63 (s, CO).

5. Crystallographic studies

Single crystals suitable for X-ray studies were obtained for compounds **3**, **4**, **7** and **9**. The first two were isolated by crystallization of an *n*-butylic ether–hexane solution, at −30 °C and the latter two by crystallization of an acetone–hexane solution. A summary of relevant crystallographic results is listed in Table 5. Diffraction data were collected on a Bruker APEX diffractometer, using a graphite monochromatized Mo–K_α radiation ($\lambda = 0.71073$ Å). An absorption correction was applied using SADABS. The structures where solved by direct methods. Refinement was carried out by full-matrix least-squares analysis with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed into calculated positions and refined using a riding model with a fixed isotropic thermal parameters. Calculations were carried out with SMART software for data collection and data reduction and SHELXTL for solution and refinement [28].

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 198370–198373 for **3**, **4**, **7** and **9**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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