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Group 6 carbene complexes derived from lithiated azoles and the crystal structure of a molybdenum thiazolinylidene complex

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Abstract

Fischer-type (alkoxy)azolyl carbene complexes and Öfele–Lappert-type azolylinylidene complexes were synthesised by reaction of 1-phenylpyrazol-3-yllithium, 4-methylthiazol-2-yllithium, benzothiazol-2-yllithium, 1-methylimidazol-2-yllithium with $M(CO)_5L$ (L = CO, THF or Cl^-; M = Cr, Mo or W) and subsequent alkylation with $CF_3SO_3CH_3$. The alkylation of Fischer-type carbene complexes containing an azolyl as the organic substituent proceeded via ring opening of tetrahydrofuran. When the alkylation is carried out in THF, the carbocation $CH_3O(CH_2)_4^+$ acts as an electrophile. Protonation rather than alkylation of coordinated imidazolyl furnished cyclic imine complexes. Changing the donor atom of a coordinated thiazole from N to C by deprotonation and alkylation afforded a carbene complex. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbene complexes; Group 6 metals; Azolinylidene complexes; Transmetallation

1. Introduction

The chemistry of carbene complexes has developed rapidly since the notion of a metal–carbon double bond was first postulated [1]. A great variety of preparative routes has afforded several hundreds of compounds, some of which are valuable in both organic syntheses and in catalytic processes [2]. Nevertheless, the development of new methodologies towards preparation of carbene complexes remains an important synthetic endeavour. The synthesis of carbene complexes derived from heterocyclic compounds continues to attract a great deal of attention [3] and these compounds have emerged as useful precursors in catalysis [4].

The majority of the Group 6 metal carbonyl carbene complexes have been synthesised by the functionalisation of a coordinated carbonyl ligand. The resulting anionic acyllithium compounds are then treated with electrophiles to afford classic Fischer-type hydroxy or alkoxycarbene products [5,6]. The preparation of heterocyclic Group 6 carbonyl carbene complexes by other synthetic routes has been reported initially by both Öfele and co-workers [7–9] and Lappert and co-workers [10,11], and more recently by others [12,13]. Earlier work in our laboratory has indicated an approach to prepare tungsten azolylinylidene complexes [14] that is probably more flexible than the method originally used by Lappert. Our transmetallation route utilises an anionic metal carbonylhalide and a lithiumazolyl compound as opposed to the conventional metal hexacarbonyl and electron-rich alkene reagents. Azolyls could, however, also react with a carbonyl ligand in the Fischer manner and we thus embarked on a study to compare and contrast the preferential formation of Fischer-type or Öfele–Lappert-type carbene complexes from simple azolyllithium and pyrazolyllithium precursors, when brought into contact with metal hexacarbonyl complexes. In addition, anionic metalcarbonyl halides and substituted carbonyl complexes $M(CO)_5(THF)$ (M = Cr, W) were used as the transition metal sources.

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2. Results and discussion

The analytical and physical data for the products are presented in Table 1 and the spectroscopic results appear in Table 2. Previously described complexes have been identified by comparison of their melting points and spectral data with known values and have been omitted from the tables. The Li^+ and $CF_3SO_3^-$ counterions are not shown in the schemes.

2.1. Synthesis and characterisation of 1-phenylpyrazolyl Group 6 carbene complexes *1*–*6*

Reaction of lithiated 1-phenylpyrazole with $M(CO)_6$ (M = Cr, Mo or W) and subsequent alkylation in CH_2Cl_2 afforded the three Fischer-type complexes **1**, **2** and **3** (Scheme 1). Performing the alkylation in tetrahydrofuran (THF) also yielded complexes **1**–**3** and simultaneously, the complexes **4**, **5** and **6** that have been O-alkylated by a butoxy(methoxy) group. Recrystallisation afforded air- and moisture-sensitive dark red, needle-like crystals of **1**–**3** and brown–red crystals of **4**–**6**.

We rationalized the unexpected formation of **4**–**6** in terms of generating a new electrophilic centre by nucleophilic attack of an oxygen lone pair in THF on the polarised CH_3 group in methyltriflate. In turn, the oxy-anion of the acylmetallate performs a nucleophilic attack on the α-carbon of the THF ring leading to heterolytic cleavage and the formation of the butoxy(methoxy)organo carbene complex (Scheme 2). To determine the role of the heterocyclic system in this event, methyl- and phenyllithium were also employed as reactants. No THF ring opening occurred, showing that the electron-withdrawing effect of the heterocyclic ring is necessary to partly suppress total acylate alkylation by CH_3^+. A contributing structure such as (c) in Scheme 2 is lacking in the alkyl and aryl carbene complexes and direct complex alkylation occurs.

^{13}C-{^1H}-NMR spectra of complexes **1**–**3** (Table 2) exhibited shifts for the aromatic carbons of 1-phenylpyrazolyl between δ 107–155, which is somewhat downfield from the resonances (δ 107–140) in the free pyrazole [15,16]. The presence of far-downfield resonances for complexes **1**, **2** and **3** at δ 263.1, δ 317.6 and δ 299.7 as well as the absence of a signal for H^5 in the ^1H-NMR spectra, confirms the presence of the carbene carbons situated at C^5.

^{13}C-{^1H}-NMR spectra of complexes **4**–**6** (Table 2) display analogous aromatic carbon shifts to complexes **1**–**3** and the carbene carbon resonances appear at δ 263.3, δ 315.7 and δ 298.9, respectively. Note the relatively large chemical shift in the molybdenum compound. Carbene complexes similar to complexes **4**–**6** have been reported in a patent [17], but no characterisation data are available.

Cis and *trans* isomers of tungsten aminocarbene complexes at room temperature [18] and of alkoxycarbene

Table 1
Analytical and physical data

Complex	m.p. (°C)	Colour	Analysis (%) [a]		
			C	H	N
1	67–68	Dark red	50.5 (50.8)	2.6 (2.7)	7.2 (7.4)
2	68–69	Dark red	45.7 (45.5)	2.3 (2.4)	6.8 (6.6)
3	66–67	Dark red	37.9 (37.7)	1.7 (2.0)	5.5 (5.5)
4	87–88	Brown–red	53.0 (53.4)	3.8 (4.0)	6.1 (6.2)
5	88–89	Brown–red	48.7 (48.6)	3.6 (3.7)	5.5 (5.7)
6	86–87	Brown–red	41.0 (41.3)	3.0 (3.1)	4.4 (4.8)
7	63–64	Dark red	49.4 (49.0)	3.5 (3.4)	3.5 (3.2)
8	79–80	Dark brown	44.9 (44.6)	3.0 (3.1)	2.8 (2.9)
9	53 [b]	Dark red	37.9 (37.7)	2.2 (2.6)	2.3 (2.4)
10	62–63	Dark red	44.2 (44.4)	3.6 (3.7)	3.3 (3.5)
11	83 [b]	Red	45.2 (45.6)	1.7 (1.9)	3.8 (3.8)
12	85 [b]	Brown	33.2 (33.6)	1.6 (1.4)	2.9 (2.8)
16	58–59 [b]	Yellow	39.8 (39.5)	2.0 (2.2)	10.4 (10.2)
17	63–64 [b]	Yellow	26.3 (26.6)	1.7 (1.5)	6.8 (6.9)
18	90–91	Pale yellow	34.1 (34.4)	2.7 (2.9)	3.9 (4.0)
20	90–91	Yellow	33.5 (33.0)	1.6 (1.5)	3.0 (3.0)
21	89 [b]	Yellow	37.4 (37.2)	1.54 (1.7)	4.6 (4.8)
22	75–76	Pale yellow	39.7 (39.4)	2.5 (2.3)	4.8 (4.6)
23	91–92	Yellow	39.6 (39.4)	2.1 (2.3)	4.6 (4.6)

[a] Required values given in parentheses.
[b] Decomposition without melting.

Table 2
Spectroscopic data

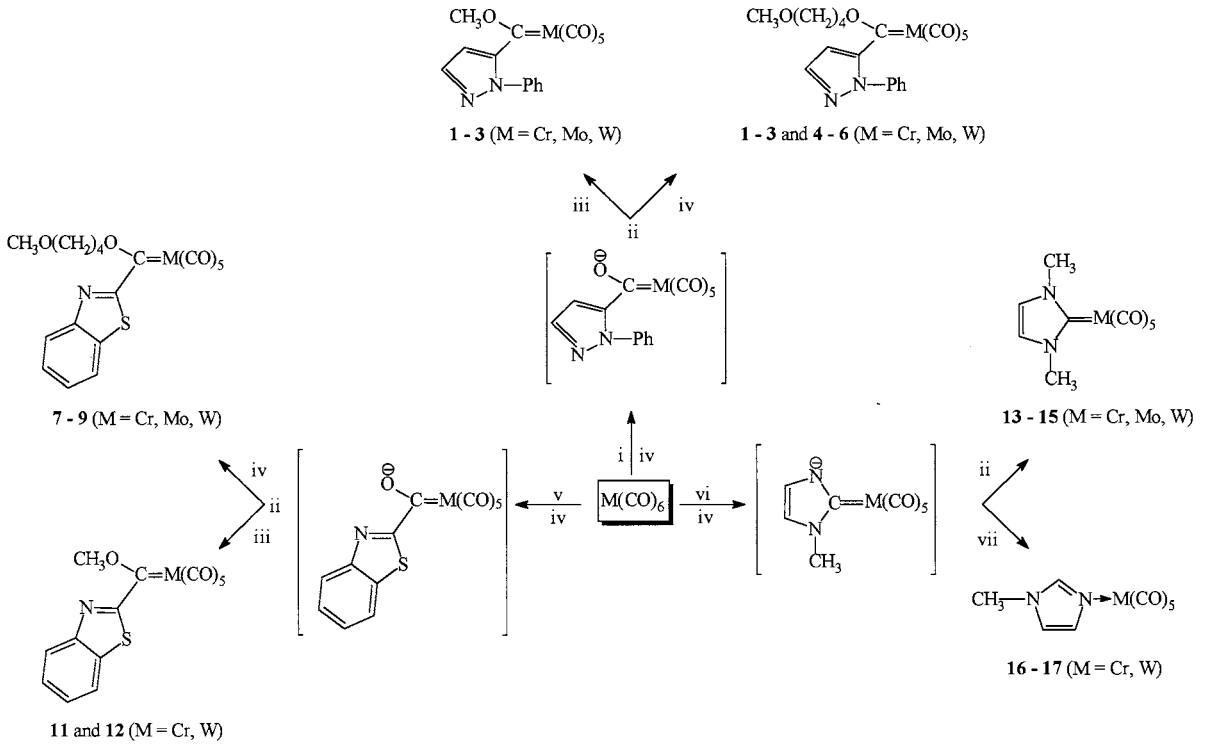
Complex		
1	δ_H [a]	7.63–7.18 (7H, m, aromatic protons), 4.38 (3H, s, OCH_3)
	δ_C [a]	263.1 (Cr = C), 215.9 (CO_{trans}), 213.5 (CO_{cis}), 152.8–115.6 (aromatic carbons), 66.4 (OCH_3)
	m/z [b]	378 ($[M]^+$, 4), 350 ($[M-CO]^+$, 44), 294 ($[M-3CO]^+$, 41), 266 ($[M-4CO]^+$, 61), 238 ($[M-5CO]^+$, 71), 223 ($[Cr\{C(O)(\overline{CN(Ph)N=CHCH})\}]^+$, 73), 52 ($[Cr]^+$, 43)
	ν (CO) [c]	2064 (s), 1988(w), 1967 (sh), 1952 (vs)
2	δ_H [a]	7.70–7.18 (7H, m, aromatic protons), 4.35 (3H, s, OCH_3)
	δ_C [a]	317.6 (Mo = C), 212.7 (Co_{trans}), 205.3 (CO_{cis}), 153.4–107.5 (aromatic carbons), 67.9 (OCH_3)
	m/z [b]	422 ($[M]^+$, <30), 394 ($[M-CO]^+$, <30), 338 ($[M-3CO]^+$, 63), 310 ($[M-4CO]^+$, 41), 282 ($[M-5CO]^+$, 36), 267 ($[Mo\{C(O)(\overline{CN(Ph)N=CHCH}\}]^+$, 29), 96 ($[Mo]^+$, 41)
	ν (CO) [c]	2072 (s), 1998 (w), 1975 (sh), 1960 (vs)
3	δ_H [a]	7.58–7.10 (7H, m, aromatic protons), 4.30 and 4.20 (3H, 2 × s, OCH_3, J = 21.0)
	δ_C [a]	299.7 (W=C), 205.3 (Co_{trans}, d, $J(^{183}W-^{13}C)$ = 125.0), 196.8 (CO_{cis}, d, $J(^{183}W-^{13}C)$ = 64.3), 155.7–117.3 (aromatic carbons), 68.7 and 67.9 (OCH_3)
	m/z [b]	510 ($[M]^+$, <15), 482 ($[M-CO]^+$, <15), 426 ($[M-3CO]^+$, 100), 398 ($[M-4CO]^+$, <14), 370 ($[M-5CO]^+$, 46), 355 ($[W\{C(O)(\overline{CH(Ph)N=CHCH})\}]^+$, 21)
	ν (CO) [c]	2072 (s), 1992 (w), 1972 (sh), 1956 (vs)
4	δ_H [a]	7.57–7.12 (7H, m, aromatic protons), 4.67 (2H, t, H^1, $J(H^1-H^2)$ = 6.1), 3.20 (3H, s, OCH_3), 3.13 (2H, t, H^4, $J(H^4-H^3)$ = 5.8), 1.37–1.18 (4H, 2 × m, H^2 and H^3)
	δ_C [a]	263.3 (Cr=C), 223.3 (CO_{trans}), 216.0 (CO_{cis}), 152.9–115.6 (aromatic carbons), 81.1 (C^1), 71.7 (C^4), 58.5 (OCH_3), 25.6 (C^2 and C^3)
	m/z [b]	450 ($[M]^+$, 4), 366 ($[M-3CO]^+$, 12), 338 ($[M-4CO]^+$, 4), 310 ($[M-5CO]^+$, 50), 77 ($[Ph]^+$, 15), 52 ($[Cr]^+$, 100)
	ν (CO) [c]	2064 (s), 1985 (w), 1965 (sh), 1956 (vs)
5	δ_H [a]	7.58–7.14 (7H, m, aromatic protons), 4.63 and 4.52 (2H, 2 × t, H^1, $J(H^1-H^2)$ = 8.0), 3.24 and 3.20 (3H, 2 × s, OCH_3), 3.13 (2H, t, H^4, $J(H^4-H^3)$ = 7.9), 1.38–1.17 (4H, 2 × m, H^2 and H^3)
	δ_C [a]	315.7 (Mo=C), 212.9 (CO_{trans}), 205.4 (CO_{cis}), 153.4–114.7 (aromatic carbons), 83.2 (C^1)
	m/z [b]	494 ($[M]^+$, <5), 412 ($[M-3CO]^+$, <5), 356 ($[M-5CO]^+$, <5)
	ν (CO) [c]	2071 (s), 1994 (w), 1956 (vs), 1922 (sh)
6	δ_H [a]	7.62–7.16 (7H, m, aromatic protons), 4.68 and 4.58 (2H, 2 × t, H^1, $J(H^1-H^2)$ = 6.0), 3.25 (3H, s, OCH_3), 3.16 (2H, t, H^4, $J(H^4-H^3)$ = 5.7), 1.36–1.23 (4H, 2 × m, H^2 and H^3)
	δ_C [a]	298.9 (W=C), 205.4 (CO_{trans}, d, $J(^{183}W-^{13}C)$ = 124.7), 196.9 (CO_{cis}, d, $J(^{183}W-^{13}C)$ = 64.2), 155.8–117.2 (aromatic carbons), 83.3 and 82.7 (C^1), 71.7 (C^4), 58.5 (OCH_3), 25.6 and 25.4 (C^2 and C^3)
	m/z [b]	582 ($[M]^+$, <1), 498 ($[M-3CO]^+$, 5), 143 ($[M-5CO]^+$, 5), 77 ($[Ph]^+$, 5)
	ν (CO) [c]	2071 (s), 1955 (vs)
7	δ_H [a]	8.24–7.50 (4H, m, aromatic protons), 5.32 (2H, t, $H^{1'}$, $J(H^{1'}-H^{2'})$ = 6.3), 3.52 (2H, t, $H^{4'}$, $J(H^{4'}-H^{3'})$ = 6.1), 3.37 (3H, s, OCH_3), 2.19 (2H, m, $H^{2'}$), 1.90 (2H, m, $H^{3'}$)
	δ_C [a]	322.9 (Cr=C), 225.9 (CO_{trans}), 216.7 (CO_{cis}), 171.4 (C^2), 153.9 (C^9), 135.1 (C^8), 128.1 (C^5), 126.8 (C^6), 125.7 (C^4), 122.3 (C^7), 80.7 ($C^{1'}$), 71.9 ($C^{4'}$), 58.6 (OCH_3), 26.7 ($C^{2'}$), 26.2 ($C^{3'}$)
	m/z [b]	441 ($[M]^+$, 3), 413 ($[M-CO]^+$, 9), 329 ([M−4CO], 9), 301 ([M−5CO], 100), 52 ($[Cr]^+$, 99), 45 ($[HCS]^+$, 35)
	ν (CO) [c]	2066 (m), 2007 (w), 1979 (s, sh), 1958 (vs)
8	δ_H [a]	8.24–7.51 (4H, m, aromatic protons), 5.17 (2H, t, $H^{1'}$, $J(H^{1'}-H^{2'})$ = 6.3), 3.51 (2H, t, $H^{4'}$, $J(H^{4'}-H^{3'})$ = 6.1), 3.37 (3H, s, OCH_3), 2.18 (2H, m, $H^{2'}$), 1.88 (2H, m, $H^{3'}$)
	δ_C [a]	313.0 (Mo=C), 214.7 (CO_{trans}), 206.0 (CO_{cis}), 172.6 (C^2), 153.9 (C^9), 135.3 (C^8), 128.0 (C^5), 126.8 (C^6), 125.7 (C^4), 122.3 (C^7), 82.3 ($C^{1'}$), 71.9 ($C^{4'}$), 58.6 (OCH_3), 26.5 ($C^{2'}$), 26.2 ($C^{3'}$)
	m/z [b]	485 ($[M]^+$, 1), 457 ($[M-CO]^+$, 3), 401 ($[M-3CO]^+$, 5), 373 ($[M-4CO]^+$, 2), 345 ($[M-5CO]^+$, 2), 96 ($[Mo]^+$, 63), 45 ($[HCS]^+$, 93)
	ν (CO) [c]	2073 (m), 2007 (w), 1978 (s, sh), 1958 (vs)
9	δ_H [a]	8.25–7.52 (4H, m, aromatic protons), 5.18 and 5.04 (2H, 2 × t, $H^{1'}$, $J(H^{1'}-H^{2'})$ = 6.6), 3.51 (2H, t, $H^{4'}$, $J(H^{4'}-H^{3'})$ = 6.2), 3.37 (3H, s, OCH_3), 2.17 (2H, m, $H^{2'}$), 1.88 (2H, m, $H^{3'}$)
	δ_C [a]	295.9 (W=C), 205.2 (CO_{trans}), 197.3 (CO_{cis}, d, $J(^{183}W-^{13}C)$ = 127), 175.1 (C^2), 153.9 (C^9), 135.4 (C^8), 128.1 (C^5), 126.9 (C^6), 125.8 (C^4), 122.4 (C^7), 83.0 ($C^{1'}$), 71.9 ($C^{4'}$), 58.6 (OCH_3), 26.4 ($C^{2'}$), 26.3 ($C^{3'}$)
	m/z [b]	573 ($[M]^+$, 1), 545 ($[M-CO]^+$, 3), 489 ($[M-3CO]^+$, 2), 433 ($[M-5CO]^+$, 3), 45 ($[HCS]^+$, 100)
	ν (CO) [c]	2074 (m), 2003 (w), 1974 (s, sh), 1954 (vs)
10	δ_H [a]	7.14 (1H, s, H^5), 5.22 (2H, t, J = 6.3, $H^{1'}$), 3.48 (2H, t, J = 6.1, $H^{4'}$) 3.34 (3H, s, OCH_3), 2.55 (3H, s, $NCCH_3$), 2.12 (2H, m, $H^{2'}$), 1.83 (2H, m, $H^{3'}$)
	δ_C [a]	320.0 (Cr=C), 225.6 (CO_{trans}), 217.0 (CO_{cis}), 172.0 (C^2), 156.5 (C^4), 119.0 (C^5), 80.2 ($C^{1'}$), 72.0 ($C^{4'}$), 58.6 (OCH_3), 26.7 ($C^{2'}$), 26.2 ($C^{3'}$), 14.0 ($NCCH_3$)
	m/z [b]	405 ($[M]^+$, 10), 377 ($[M-CO]^+$, 16), 293 ($[M-4CO]^+$, 14), 265 ($[M-5CO]^+$, 100)
	ν (CO) [c]	1065 (m), 2004 (w), 1976 (s, sh), 1955 (vs)

Table 2 (Continued)

Complex		
11	δ_H [a]	8.26–7.53 (4H, m, aromatic protons), 5.02 (3H, s, OCH_3)
	δ_C [a]	324.9 (Cr=C), 225.8 (CO_{trans}), 216.7 (CO_{cis}), 171.1 (C^2), 153.9 (C^9), 135.2 (C^8), 128.1 (C^5), 126.8 (C^6), 125.8 (C^4), 122.4 (C^7), 66.8 (OCH_3)
	m/z [b]	369 ($[M]^+$, 4), 341 ($[M-CO]^+$, 11), 313 ($[M-2CO]^+$, 8), 285 ($[M-3CO]^+$, 22), 257 ($[M-5CO]^+$, 31), 229 ($[M-5CO]^+$, 81), 52 ($[Cr]^+$, 100), 45 ($[HCS]^+$, 4)
	ν (CO) [c]	2067 (m), 2009 (w), 1983 (s, sh), 1954 (vs)
12	δ_H [a]	8.25–7.53 (4H, m, aromatic protons), 4.88 and 4.76 (3H, 2 × s, OCH_3)
	δ_C [a]	297.7 (W=C), 205.1 (CO_{trans}), 197.2 (CO_{cis}, d, $J(^{183}W-^{13}C) = 125.5$), 174.9 ($C^2$), 153.9 ($C^9$), 135.5 ($C^8$), 128.1 ($C^5$), 127.0 ($C^6$), 125.8 ($C^4$), 122.5 ($C^7$), 69.2 ($OCH_3$)
	m/z [b]	501 ($[M]^+$, 1), 473 ($[M-CO]^+$, 43), 445 ($[M-2CO]^+$, 39), 417 ($[M-3CO]^+$, 65), 389 ($[M-4CO]^+$, 62), 318 ($[W\{\overline{C{=}NC_6H_4S}\text{-}o\}]^+$, 87)
	ν (CO) [c]	2075 (m), 2005 (w), 1977 (s, sh), 1956 (vs)
16	δ_H [a]	7.36 (1H, s, H^2), 6.84 (2H, 2 × s, H^4 and H^5), 3.67 (3H, s, NCH_3)
	δ_C [a]	220.6 (CO_{trans}), 215.1 (CO_{cis}), 141.0 (C^2), 134.4 (C^4), 121.3 (C^5), 34.1 (NCH_3)
	m/z [b]	274 ($[M]^+$, 14), 246 ($[M-CO]^+$, 4), 218 ($[M-2CO]^+$, 2), 190 ($[M-3CO]^+$, 5), 162 ($[M-4CO]^+$, 28), 134 ($[M-5CO]^+$, 89), 52 ($[Cr]^+$, 90)
	ν (CO) [c]	2065 (w), 1929 (vs)
17	δ_H [a]	7.58 (1H, s, H^2), 7.04 (1H, m, H^4), 6.83 (1H, s, H^5), 3.72 (3H, s, NCH_3)
	δ_C [a]	202.6 (CO_{trans}), 198.6 (CO_{cis}, $J(^{183}W-^{13}C) = 43$), 142.6 (C^2), 135.4 (C^4), 121.7 (C^5), 34.1 (NCH_3)
	m/z [b]	406 ($[M]^+$, < 5), 350 ($[M-2CO]^+$, 8), 322 ($[M-3CO]^+$, 13), 294 ($[M-4CO]^+$, 7), 266 ($[M-5CO]^+$, 15), 183 ($[W]^+$, 15)
	ν (CO) [c]	2071 (m), 1933 (vs), 1916 (sh)
18	δ_H [a]	6.97 (1H, s, H^5), 4.03 (3H, s, NCH_3), 2.43 (3H, s, $NCCH_3$)
	δ_C [a]	220.7 (Mo=C), 212.5 (CO_{trans}), 206.5 (CO_{cis}), 145.7 (C^4), 120.3 (C^5), 41.7 (NCH_3), 15.0 ($NCCH_3$)
	m/z [b]	349 ($[M]^+$, 37), 321 ($[M-CO]^+$, 15), 293 ($[M-2CO]^+$, 21), 265 ($[M-3CO]^+$, 32), 237 ($[M-4CO]^+$,76), 209 ($[M-5CO]^+$, 79), 169 ($[Mo\{S{=}C{=}N{=}(CH_3)\}]^+$, 49)
	ν (CO) [c]	2067 (m), 1985 (w), 1945 (vs), 1945 (vs)
20	δ_H [a]	7.71 (1H, m, H^4), 7.60 (1H, m, H^7), 7.62–7.38 (2H, m, H^5 and H^6), 4.27 (3H, s, NCH_3)
	δ_C [a]	218.1 (W=C), 202.0 (Co_{trans}), 197.2 (CO_{cis}, $J(^{183}W-^{13}C) = 125.7$), 144.6 ($C^9$), 136.9 ($C^8$), 127.0 ($C^5$), 125.3 ($C^6$), 120.9 ($C^4$), 113.7 ($C^7$), 41.6 ($NCH_3$)
	m/z [b]	473 ($[M]^+$, 78), 445 ($[M-CO]^+$, 15), 417 ($[M-2CO]^+$, 39), 389 ($[M-3CO]^+$, 99), 361 ($[M-4CO]^+$, 95), 333 ($[M-5CO]^+$, 100), 318 ($[W\{\overline{C{=}NC_6H_4S}\text{-}o\}]^+$, 12)
	ν (CO) [c]	2067 (m), 1982 (w), 1940 (vs), 1940 (vs)
21	δ_H [a]	8.89 (1H, s, H^2), 7.08 (1H, s, H^5), 2.59 (3H, s, NCH_3)
	δ_C [a]	220.7 (CO_{trans}), 214.5 (CO_{cis}), 157.2 (C^4), 156.0 (C^2), 116.0 (C^5), 18.6 ($NCCH_3$)
	m/z [b]	291 ($[M]^+$, 7), 207 ($[M-3CO]^+$, 3), 179 ($[M-4CO]^+$, 12), 151 ($[M-5CO]^+$, 44), 99 ($[\overline{C{=}NC(CH_3){=}CHS}]^+$, 100)
	ν (CO) [c]	2070 (w), 1943 (vs), 1924 (s, sh)
22	δ_H [a]	8.70 (1H, s, H^2), 2.45 (3H, s, $NCCH_3$), 2.36 (3H, s, $SCCH_3$)
	δ_C [a]	220.8 (CO_{trans}), 214.5 (CO_{cis}), 153.1 (C^4), 151.1 (C^2), 128.3 (C^5), 16.1 ($NCCH_3$), 12.4 ($SCCH_3$)
	m/z [b]	305 ($[M]^+$, 7), 277 ($[M-CO]^+$, 3), 249 ($[M-2CO]^+$, 3), 221 ($[M-3CO]^+$, 4), 193 ($[M-4CO]^+$, 15), 165 ($[M-5CO]^+$, 79), 113 ($[\overline{C{=}NC(CH_3){=}C(CH)_3S}]+$, 100), 52 ($[Cr]^+$, 76)
	ν (CO) [c]	2069 (w), 1942 (vs), 1923 (s, sh)
23	δ_H [a]	6.97 (1H, s, H^5), 4.04 (3H, s, NCH_3), 2.43 (3H, s, $NCCH_3$)
	δ_C [a]	227.2 (C^2) 222.2 (CO_{trans}), 217.0 (CO_{cis}), 146.6 (C^4), 120.1 (C^5), 40.7 (NCH_3), 15.1 ($NCCH_3$)
	m/z [b]	305 ($[M]^+$, 43), 277 ($[M-CO]^+$, 22), 249 ($[M-2CO]^+$, 17), 221 ($[M-3CO]^+$, 25), 193 ($[M-4CO]^+$, 50), 165 ($[M-5CO]^+$, 99),84 ($[CrS]^+$), 52 ($[Cr]^+$, 100)
	ν (CO) [c]	2060 (m), 1981 (w), 1938 (vs)

[a] Measured in $CDCl_3$, coupling constants in Hz.
[b] Coupling constants in Hz, intensities given relative to strongest peak.
[c] Measured in hexane.

complexes at much lower temperatures have been reported [19]. This phenomenon is now also evident in the ^{1}H-NMR spectra of complexes **3** and **6** at room temperature, in the form of two sets of separate peaks for both the OCH_3 and OCH_2 protons, respectively. The intensities of the peaks for related isomers are approximately the same, suggesting that they occur in roughly a 1:1 ratio. The failure to observe this phe-



Scheme 1. Reagents: (i) LiCN(Ph)N=CHCH; (ii) $CF_3SO_3CH_3$; (iii) CH_2Cl_2; (iv) THF; (v) LiC=NC_6H_4S-*o*; (vi) LiC=NCH=CHN(CH_3); (vii) CF_3SO_3H.

nomenon before can only be ascribed to the lower resolution NMR spectrometers used when the original studies were performed. The coupling constants between the *cis* and *trans* carbonyl groups and ^{183}W for complexes **3** and **6** in the ^{13}C-{^1H} NMR spectra could be calculated, but the signals corresponding to the coupling intensities between the carbene carbon and ^{183}W were very weak.

The A_1^2 peak in the infrared spectra of all six complexes occurs as a shoulder at a higher frequency than the E vibration. With the exception of complex **6**, the forbidden B_1 peak indicates that the 1-phenylpyrazolyl moiety causes distortion of the carbonyls from idealised C_{4v} symmetry.

2.2. Synthesis and characterisation of 4-methylthiazolyl (10) and benzothiazolyl alkoxycarbene complexes (7 to 9, 11 and 12) of the Group 6 metals

It is mentioned here that the complex $(CO)_5Cr[C\{O(CH_2)_4OCH_3\}\{C{=}NC(CH_3){=}CHS\}]$ (**10**) was obtained as a by-product in the attempted reaction between a neutral chromium pentacarbonyl complex $[Cr(CO)_5(THF)]$, and 4-methylthiazol-2-yllithium. Its formation is ascribed to the incomplete conversion of $[Cr(CO)_6]$ to $[Cr(CO)_5(THF)]$, as well as to the presence of the THF-derived alkylation agent involved in the formation of complexes **4**–**9** (vide supra). The structure is supported by MS, IR, ^1H- and ^{13}C-{^1H} NMR results.

Reaction of lithiated benzothiazole with $M(CO)_6$ (M = Cr, Mo or W) and subsequent alkylation in THF afforded complexes **7**–**9** and **11** and **12**. Performing the alkylation in CH_2Cl_2 gave **11** and **12** exclusively. The same THF ring-opening mechanism as discussed for complexes **4**–**6** is again applicable to the formation of complexes **7**–**9**. We have not been able to isolate the molybdenum analogue in analytically pure form. The characterisation data for the complexes (Table 2) confirm their structural assignments.

2.3. Interaction of a lithiated imidazole with $M(CO)_6$ (M = Cr, Mo, W)

Group 6 carbene complexes derived from imidazole derivatives have formerly been reported by Öfele and co-workers [7,9], who used $HCr(CO)_5^-$ as source of metal carbonyl. The synthesis of Fischer-type carbene complexes using 1-methylimidazol-2-yllithium as nucleophilic reagent has, however, not been mentioned before. Addition of $M(CO)_6$ (M = Cr, Mo or W) to a THF solution of 1-methylimidazol-2-yllithium, followed by methylation now also yielded only the Öfele–Lappert-type complexes **13**–**15**. Although these three complexes are known and fully characterised [9], this route to 1,3-dimethylimidazol-2-inilidene has not been utilised before and leaves the option of protonation rather than alkylation in the first step. Such a procedure, however, afforded the new imino complexes **16** and **17**. Matching

results have already been obtained in our laboratory [14,20] where, as in this event, it is implied that the most stable thermodynamic product appears to favour C-protonation and N-coordination. The structures proposed were based on elemental analysis as well as conclusive spectral data including mass spectrometry.

2.4. Interaction of a thiazolyllithium with $M(CO)_5(THF)$

$M(CO)_5R^-$ complexes (R = alkyl, aryl) of the Group 6 metals usually do not form on addition of organolithium compounds to $M(CO)_5(THF)$. In the carbanion 4-methylthiazol-2-yllithium, the negative charge could be effectively delocalised onto the N-atom and such a substitution seemingly becomes possible. Treatment of a solution of 4-methylthiazol-2-yllithium with $M(CO)_5(THF)$ (M = Mo, W) followed by methylation in CH_2Cl_2 and chromatographic purification, yielded the pure complexes **18** and **19**. A similar procedure with benzothiazol-2-yllithium and $W(CO)_5(THF)$ afforded complex **20** (Scheme 3). These three heterocyclic carbene complexes could thus be synthesised via this route employing milder conditions than the previously described method [10].

The spectroscopic data for complex **19**, previously produced by halide substitution from $[W(CO)_5Cl]^-$ [14], and data for the other new compounds are in line with their proposed structures.

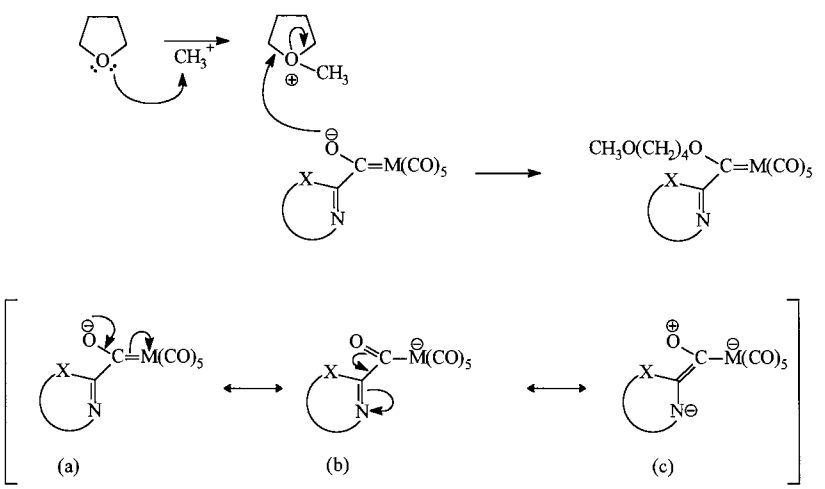
2.5. Rearrangement of an N-coordinated thiazole during consecutive lithiation and alkylation

We have indicated above that a C-coordinated imidazolyl converts into the N-coordinated form (**16**, **17**) during protonation. One could ask whether an N-coordinated azole would change into the C-coordinated form upon deprotonation. The experiment conducted involved the chromium thiazole complex **21**. Previous reports of coordinated thiazoles have indicated the possibility of both N- and S-coordination [21]. In this case however, only N-coordination was evident from NMR analysis, as has been observed before [22] in the synthesis of the benzothiazole analogue of this complex.

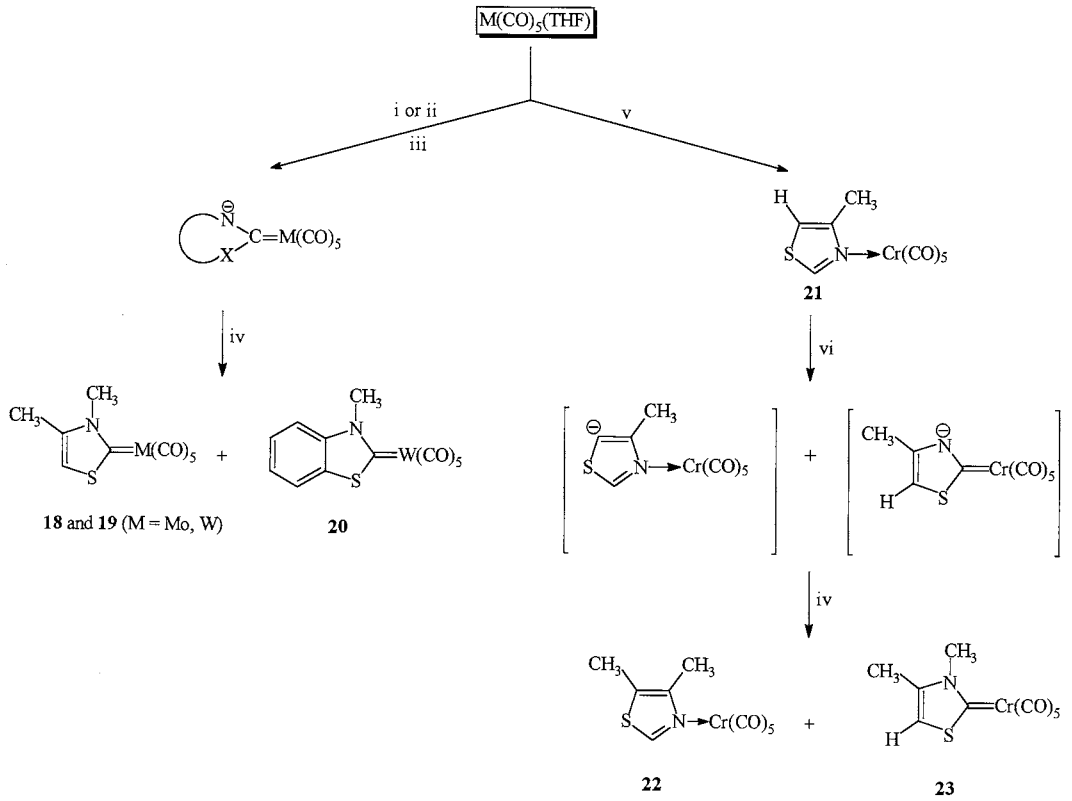
Treatment of **21** with BuLi, followed by methylation and chromatographic purification afforded **22** as pale yellow and **23** as yellow crystals. The parallel formation of these two complexes in a ratio of ca. 1:3 indicates the exceptional stability of the C-coordinated anion and the acidity of the proton at C^4 that competes for the butyl anion with the C^2 proton in the N-coordinated form **21**. We are now utilising the second result in a modified form by initially blocking the C^2 position with CH_3 or SCH_3.

2.6. An alternative method for the preparation of compounds *13* and *15* and for preparing the known related bis(carbene) complexes (*24* and *25*)

Substitution of halide in $M(CO)_5X^-$ compounds by lithiated azoles, followed by alkylation, is known to produce carbene complexes [14]. Since all the complexes have been described before [9,23], we mention that such a transmetallation of 2-lithiated 1-methylimidazole (Scheme 4) furnished both the mono carbene complexes **13** and **15** and the bis(carbene) complexes **24** and **25** albeit in fairly low yields. Imidazolyls are the only azolyls we know of that furnish bis(carbene) complexes in addition to the mono(carbene) complexes.



Scheme 2. THF heterolytic ring cleavage.



Scheme 3. Reagents: (i) LiC=NC(CH$_3$)=CHS; (ii) LiC=NC$_6$H$_4$S-*o*; (iii) THF; (iv) CF$_3$SO$_3$CH$_3$; (v) CH=NC(CH$_3$)=CHS; (vi) BuLi.

3. Crystal structure of [(CO$_5$)Mo{CN(CH$_3$)C(CH$_3$)=CHS}] (18)

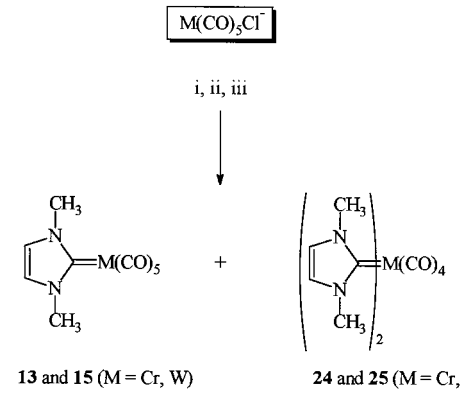
Selected bond lengths (Å) and angles (°) for **18** are given in Table 3.

The six ligands form an octahedral configuration around the central Mo atom (Fig. 1). The bond to the carbonyl ligand trans to the thiazolyl ligand (1.955 Å) is 0.04 Å shorter than the other (*cis*) metal–carbonyl bonds (2.039 Å). In line with these results, a search of the Cambridge Structural Database [24] for pentacarbonyl molybdenum complexes yielded 93 structures, with an average bond length of the opposing carbonyl of 1.992 Å, while the average bond lengths for the other carbonyls were longer, namely 2.048 Å. Such structures show a tendency towards an inverse relationship between the Mo–C$_{ligand}$ and the Mo–C$_{trans}$ bond lengths, however, since there are only seven structures including the present one, it is not possible to draw a definite conclusion (Fig. 2). The fact that the C(6)–N(1) distance (1.351 Å) is shorter than that between C(8) and the nitrogen (1.393 Å) is in accordance with results for acyclic aminocarbon complexes with no free rotation around the carbon–nitrogen bond at room temperature [25].

The thiazole ligand is planar within 0.02 Å with the plane being twisted 44° from the plane through Mo, C(2), C(3), C(5) and C(6). An eclipsed conformation is thereby attained, thus minimising interactions with the carbonyl ligands.

4. Summary

Lithiated pyrazoles [14] and imidazoles substitute THF or halide ligands from M(CO)$_5$L to from azolinylidine compounds upon alkylation. With L = CO, imidazolyls afforded similar Öfele–Lappert-type carbene complexes whereas all the other azolyls studied yield Fischer-type carbene complexes. When the alkyl-



Scheme 4. Reagents: (i) LiC=NCH=CHN(CH$_3$); (ii) THF; (iii) CF$_3$SO$_3$CH$_3$.

Table 3
Selected bond lengths (Å) and angles (°) for [(CO_5Mo{$\overline{CN(CH_3)C(CH_3)=CHS}$}] (**18**)

Bond lengths			
S(1)–C(6)	1.711(3)	S(1)–C(7)	1.711(5)
Mo–C(6)	2.247(4)	N(1)–C(6)	1.351(4)
N(1)–C(8)	1.393(5)	N(1)–C(10)	1.467(5)
C(7)–C(8)	1.326(6)		
Bond angles			
C(6)–N(1)–C(8)	118.0(3)	C(6)–S(1)–C(7)	94.1(2)
C(6)–N(1)–C(10)	121.9(3)	C(8)–N(1)–C(10)	120.1(3)
N(1)–C(6)–S(1)	105.9(3)	N(1)–C(6)–Mo	133.8(2)
S(1)–C(6)–Mo	119.9(2)		

ation is carried out in THF with $CF_3SO_3CH_3$, the carbocation $CH_3O(CH_2)_4^+$ formally acts as an electrophile. Protonation of imidazolyl complexes do not afford carbene complexes but coordinated imines and consecu-tive deprotonation and alkylation of an N-coordinated thiazole leads to carbene complex formation.

5. Experimental

5.1. General

All reactions and manipulations were carried out under an atmosphere of nitrogen using standard Schlenck techniques. THF and diethyl ether were distilled under nitrogen from sodium wire and benzophenone, pentane and hexane from sodium wire and CH_2Cl_2 from CaH_2.

The compounds $[M(CO)_5Cl]^-[NEt_4]^+$ (M = Cr, W), were prepared directly before use according to a literature method [26]. Deuterated solvents, the Group 6 metal hexacarbonyls, 4-methylthiazole, benzothiazole, 1-phenylpyrazole, CF_3SO_3H, $CF_3SO_3CH_3$, (Aldrich), *n*-BuLi (Merck) and 1-methylimidazole (Fluka) were purchased and used without further purification. Flash

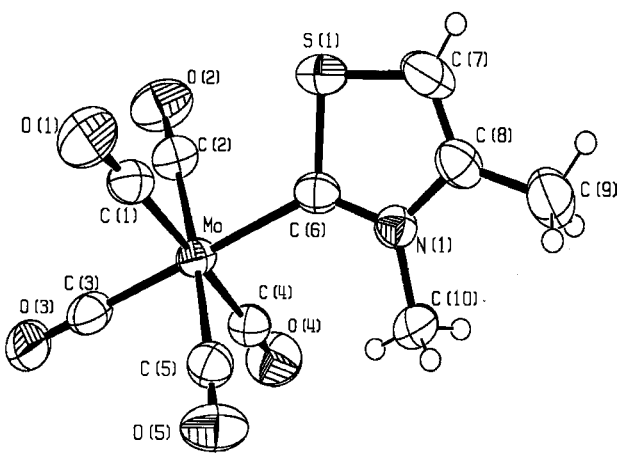


Fig. 1. ORTEP plot of **18** [(CO_5Mo{$\overline{CN(CH_3)C(CH_3)=CHS}$}].

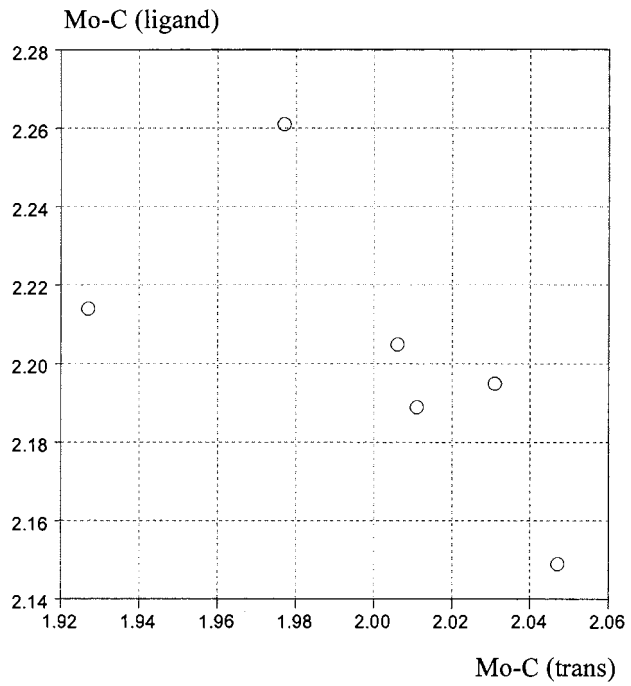


Fig. 2. Comparison of Mo–C_{ligand} and Mo–C_{trans} bond lengths.

column chromatography (FCC) was performed using Merck Kieselgel 60 (particle size 0.063–0.200 mm) washed with dry diethyl ether and dried overnight under vacuum.

Melting points were determined on a standardized Büchi 535 apparatus and infrared spectra were determined on a Perkin–Elmer 841 apparatus. Mass spectra were recorded on a Finnegan Mat 8200 instrument (electron impact at 70 eV) and NMR spectra (^{1}H-NMR at 200 MHz and ^{13}C-{^{1}H} NMR at 50 MHz) on a VXR 200 FT spectrometer. Elemental analyses were carried out by the Division of Energy Technology, CSIR, Pretoria.

5.2. Preparation of Group 6 complexes *1–6*

A solution of 1-phenylpyrazole (0.6 cm^3, 4.8 mmol) in 40 cm^3 THF at −78°C was treated with BuLi in hexane (ca. 1.6 M, 3.12 cm^3, 4.8 mmol) for 45 min. $M(CO)_6$ (M = Cr, Mo, W; 0.88 g, 1.06 g, 1.41 g, 4.0 mmol), was added in solid form to the lithium salt solution at −78°C, stirred for 2 h at this temperature and gradually warmed to room temperature (r.t.). After methylation with $CF_3SO_3CH_3$ (0.48 cm^3, 4.0 mmol) at −50°C for 30 min, the solution was slowly warmed to r.t. Removal of the solvent, washing with CH_2Cl_2 (3 × 20 cm^3) and FCC with hexane/diethyl ether (5:1.5) afforded the pure complexes (% yields: **1**, 26.4; **2**, 17.9; **3**, 29.5; **4**, 17.2; **5**, 15.9 and 6, 22.5). Recystallization at −20°C from hexane yielded air and moisture sensitive needle-like dark red and brown–red crystals of **1–3** and **4–6**, respectively.

5.3. Preparation of Group 6 complexes **7–9**

A solution of benzothiazol-2-yllithium, prepared from benzothiazole (0.33 cm^3, 3.0 mmol) in 40 cm^3 THF at −78°C and BuLi in hexane (ca. 1.6 M, 1.9 cm^3, 3.0 mmol), was slowly added to a solution of $M(CO)_6$ (M = Cr, Mo, W; 0.66, 0.79, 1.06 g, 3.0 mmol) in 50 cm^3 THF at −78°C and stirred for 2.5 h at this temperature. Upon reaching r.t., the reaction mixture was stirred for a further 30 min. Methylation with $CF_3SO_3CH_3$ (0.34 cm^3, 3.0 mmol) at −78°C, stirring overnight with gradual warming to r.t., solvent removal, washing with CH_2Cl_2 (3 × 20 cm^3) and cold FCC (−15°C) with hexane–CH_2Cl_2 (4:1; 3:1–1:2 and 2:1–3:1, respectively), afforded the pure powder-like complexes (% yields: **7**, 32; **8**, 22 and **9**, 27).

5.4. Preparation of Group 6 complexes **11** and **12**

A solution of benzothiazol-2-yllithium, prepared from benzothiazole (0.33 cm^3, 3.0 mmol) in 40 cm^3 THF at −78°C and BuLi in hexane (ca. 1.6 M, 1.9 cm^3, 3.0 mmol), was slowly added to $M(CO)_6$ (M = Cr, W; 0.66, 1.06 g, 3.0 mmol) in 50 cm^3 THF at −78°C. The solution was stirred for 3 h at this temperature, gradually warmed to r.t., the solvent removed, the residue washed with hexane (3 × 20 cm^3) and dissolved in CH_2Cl_2. Methylation with $CF_3SO_3CH_3$ (0.34 cm^3, 3.0 mmol) at −20°C for 30 min, warming to r.t., filtration through a silica plug and cold FCC (−15°C) with hexane–CH_2Cl_2 (4:1 and 5:1, respectively) afforded the pure complexes (% yields: **11**, 28 and **12**, 31). Dissolving **11** in diethyl ether, layering with hexane and cooling to −80°C produces red microcrystals of the chromium complex. Reducing the eluent volume of **12** and cooling to −20°C yields brown crystals of the tungsten complex.

5.5. Preparation of Group 6 complexes **13–15**

To a solution of 1-methylimidazol-2-yllithium, prepared from 1-methylimidazole (0.32 cm^3, 4.0 mmol) in 40 cm^3 THF at −45°C and BuLi in hexane (ca. 1.6 M, 2.6 cm^3, 4.0 mmol), solid $M(CO)_6$ (M = Cr, Mo, W; 0.88, 1.06, 1.41 g, 4.0 mmol) was added at −70°C and the solution stirred for 2 h at this temperature. The reaction mixture was slowly warmed to r.t., cooled to −50°C and protonated with $CF_3SO_3CH_3$ (0.48 cm^3, 4.0 mmol). Overnight stirring with gradual warming to r.t., solvent removal, washing with hexane (3 × 20 cm^3), filtering through a silica plug using CH_2Cl_2 and cold FCC (−20°C) using hexane–diethyl ether (1:9) afforded the pure complexes (% yields: **13**, 19.7; **14**, 23.2 and **15**, 24). Recrystallisation at −20°C from hexane yielded yellow crystals in all three cases.

5.6. Preparation of Group 6 complexes **16** and **17**

The analogous procedure using 1-methylimidazole (0.32 cm^3, 4.0 mmol), BuLi in hexane (ca. 1.6 M, 2.6 cm^3, 4.0 mmol), $M(CO)_6$ (M = Cr, W; 0.88, 1.41 g, 4.0 mmol), protonation with CF_3SO_3H (0.35 cm^3, 4.0 mmol) and cold FCC (−20°C) with hexane–diethyl ether (1:9), afforded the pure complexes (% yields: **16**, 9.52 and **17**, 11.2).

5.7. Preparation of Group 6 complexes **18** and **19**

$M(CO)_6$ (M = W, Mo; 1.06, 0.79 g, 3.0 mmol) in 100 cm^3 THF was irradiated with UV light for 3 h to prepare the corresponding $M(CO)_5$(THF) complex. A solution of 4-methylthiazol-2-yllithium, prepared from 4-methylthiazole (0.27 cm^3, 3.0 mmol) in 40 cm^3 THF at −78°C and BuLi in hexane (ca. 1.6 M, 1.9 cm^3, 3.0 mmol), was added to the $M(CO)_5$(THF) solution at −78°C and stirred for 2 h. The reaction mixture was allowed to warm slowly to r.t., stirred for a further 2 h and the THF removed in vacuo. After dissolving the residue in CH_2Cl_2, it was methylated with $CF_3SO_3CH_3$ (0.34 cm^3, 3.0 mmol) at −78°C. Overnight stirring with warming to r.t., filtration through Celite and cold FCC (−15°C) with hexane–CH_2Cl_2 (3:1) afforded the pure complexes (% yields: **18**, 36 and **19**, 44).

5.8. Preparation of Group 6 complex **20**

The analogous procedure using benzothiazole (0.33 cm^3, 3.0 mmol), BuLi in hexane (ca. 1.6 M, 1.9 cm^3, 3.0 mmol), $W(CO)_5$(THF), methylation with $CF_3SO_3CH_3$ (0.34 cm^3, 3.0 mmol) and cold FCC (−10°C) with hexane–CH_2Cl_2 (3:1), afforded the pure complex (% yield: 21). Recrystallisation from diethyl ether at −50°C produces yellow crystals of the tungsten complex.

5.9. Preparation of Group 6 complex **21**

$Cr(CO)_6$ (0.66 g, 3.0 mmol) in 100 cm^3 THF was irradiated with UV light for 3 h to prepare the corresponding $Cr(CO)_5$(THF) complex. This solution was added to 4-methylthiazole (0.27 cm^3, 3.0 mmol) in 30 cm^3 THF at r.t. and stirred for 1 h. Solvent removal, FCC with hexane–diethyl ether (7:3), reducing the eluent volume and cooling to −25°C afforded yellow crystals of the complex (% yield: 77).

5.10. Preparation of Group 6 complexes **13**, **15**, **24** and **25**

The analogous procedure using 1-methylimidazole (0.15 cm^3, 2.0 mmol), BuLi in hexane (ca. 1.6 M, 1.3 cm^3, 2.0 mmol), $[M(CO)_5Cl]^-[NEt_4]^+$ (M = Cr, W; 0.72 g, 0.98 g, 2.0 mmol), methylation with $CF_3SO_3CH_3$

(0.24 cm^3, 2.0 mmol) and FCC with hexane–CH_2Cl_2 (1:3) afforded the pure yellow complexes (% yields: **13**, 28.2; **15**, 22; **24**, 8.44 and **25**, 11.2).

5.11. Preparation of Group 6 complexes *22* and *23*

A solution of **21** (0.59 g, 2.0 mmol) in 40 cm^3 THF was treated with BuLi in hexane (ca. 1.6 M, 1.3 cm^3, 2.0 mmol) for 30 min at −78°C. The reaction mixture was slowly warmed to r.t. and treated with $CF_3SO_3CH_3$ (0.23 cm^3, 2.0 mmol) for 30 min at −50°C. Gradual warming to r.t., solvent removal, filtering through a silica plug using CH_2Cl_2 and cold FCC (−20°C) with hexane–diethyl ether (4:1) afforded the pure complexes (% yields: **22**, 8 and **23**, 26). Yellow crystals of **23** were obtained by solvent removal, washing with pentane (3×20 cm^3), dissolution in diethyl ether, layering with pentane and cooling to −25°C. Pale-yellow crystals of **22** were obtained by eluent volume reduction and cooling to −30°C.

5.12. Crystal structure determination

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 121679 for compound **18**.

Data were collected at 25°C from a yellow, regular ($0.45 \times 0.38 \times 0.35$) mm single crystal of **18** ($C_{10}H_7MoNO_5S$). An Enraf–Nonius CAD4F diffractometer with a monochromated incident beam (Mo–K_α) of wavelength $\lambda = 0.71073$ Å was used to collect the data by employing $\omega - 2\theta$ scans and over a theta range of 2.14–22.97°. Of the 2195 collected reflections, 1830 were unique and the R_{int} value is 0.0241. The crystal was found to be triclinic, space group $P\bar{1}$ with two complete chemical units per cell. The unit cell dimensions a, b, c (Å) are 7.759(1), 9.721(2), 10.172(2), respectively, and the values for α, β, γ (°) are 87.26(2), 70.15(1), 66.55(2), respectively.

A total of 192 parameters were refined with a final R value of 0.0236, ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) and R_w of 0.0608, ($R_w = [\Sigma(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0220P)^2 + 0.72P]$ where $P = (\max(F_o^2, 0) + 2F_c^2)/3$). The structure was solved by interpretation of a Patterson synthesis which yielded the position of the molybdenum and refinement was by full-matrix least squares, with all non-H atoms allowed anisotropic thermal motion. Hydrogens were placed from a difference map and refined isotropically.

SHELX-97 [27] was used to solve and refine the structures, ORTEP-3 [28] was used to generate Fig. 1, while the program VISTA v. 2.0 [24] (part of the Cambridge Crystallographic Data Centre software) was used to draw Fig. 2.

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