

# Synthesis, characterization and reactivity of the molybdenum(VI) complex $[\text{MoCl}(\text{NAr})_2(\text{CH}_2\text{CMe}_2\text{Ph})]$ ( $\text{Ar} = 2,6\text{-Pr}_2^i\text{C}_6\text{H}_3$ )

Vernon C. Gibson <sup>a</sup>, Carl Redshaw <sup>b,\*</sup>, Gary L.P. Walker <sup>a</sup>,  
William Clegg <sup>c</sup>, Mark R.J. Elsegood <sup>d</sup>

<sup>a</sup> Department of Chemistry, Imperial College, South Kensington, London SW7 2AY, UK

<sup>b</sup> Wolfson Materials and Catalysis Centre, School of Chemical Sciences and Pharmacy, The University of East Anglia, Norwich NR4 7TJ, UK

<sup>c</sup> School of Natural Sciences (Chemistry), University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK

<sup>d</sup> Chemistry Department, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK

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## Abstract

The compounds  $[\text{MoCl}(\text{NAr})_2\text{R}]$  ( $\text{R} = \text{CH}_2\text{CMe}_2\text{Ph}$  (**1**) or  $\text{CH}_2\text{CMe}_3$  (**2**);  $\text{Ar} = 2,6\text{-Pr}_2^i\text{C}_6\text{H}_3$ ) have been prepared from  $[\text{MoCl}_2(\text{NAr})_2(\text{dme})]$  ( $\text{dme} = 1,2\text{-dimethoxyethane}$ ) and one equivalent of the respective Grignard reagent  $\text{RMgCl}$  in diethyl ether. Similarly, the mixed-imido complex  $[\text{MoCl}_2(\text{NAr})(\text{NBU}^i)(\text{dme})]$  affords  $[\text{MoCl}(\text{NAr})(\text{NBU}^i)(\text{CH}_2\text{CMe}_2\text{Ph})]$  (**3**). Chloride substitution reactions of **1** with the appropriate lithium reagents afford the compounds  $[\text{MoCp}(\text{NAr})_2(\text{CH}_2\text{CMe}_2\text{Ph})]$  (**4**) ( $\text{Cp} = \text{cyclopentadienyl}$ ),  $[\text{MoInd}(\text{NAr})_2(\text{CH}_2\text{CMe}_2\text{Ph})]$  (**5**) ( $\text{Ind} = \text{Indenyl}$ ),  $[\text{Mo}(\text{OBU}^i)(\text{NAr})_2(\text{CH}_2\text{CMe}_2\text{Ph})]$  (**6**),  $[\text{MoMe}(\text{NAr})_2(\text{CH}_2\text{CMe}_2\text{Ph})]$  (**7**),  $[\text{MoMe}(\text{PMe}_3)(\text{NAr})_2(\text{CH}_2\text{CMe}_2\text{Ph})]$  (**8**) (formed in the presence of  $\text{PMe}_3$ ) and  $[\text{Mo}(\text{NHAr})(\text{NAr})_2(\text{CH}_2\text{CMe}_2\text{Ph})]$  (**9**). In the latter case, a by-product  $\{[\text{Mo}(\text{NAr})_2(\text{CH}_2\text{CMe}_2\text{Ph})]_2(\mu\text{-O})\}$  (**10**) has also been isolated. The crystal structures of **1**, **4**, **5** and **10** have been determined. All possess distorted tetrahedral metal centres with *cis* near-linear arylimido ligands; in each case (except **5**, for which the evidence is unclear) there are  $\alpha$ -agostic interactions present.

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**Keywords:** Synthesis; Bis(imido) molybdenum; Monoalkyl; Crystal structures; Agostic interactions

## 1. Introduction

We have reported the synthesis and characterization of a number of four-coordinate bis(imido) dialkyl complexes of the form  $[\text{Mo}(\text{NR}^1)(\text{NR}^2)(\text{R}^3)_2]$  ( $\text{R}^1 = \text{CMe}_3$ ,  $\text{R}^2 = 2,6\text{-Pr}_2^i\text{C}_6\text{H}_3$ ,  $\text{R}^3 = \text{CH}_2\text{CMe}_3$ ) and their subsequent reactions with phenols to yield well-defined metathesis catalysts [1a]. We have also described the mixed-imido dialkyls  $[\text{Mo}(\text{NR}^1)(\text{NR}^2)(\text{R}^3)_2]$  ( $\text{R}^1 = \text{CMe}_3$ ,  $\text{R}^2 = \text{C}_6\text{F}_5$ ,  $\text{R}^3 = \text{CH}_2\text{CMe}_2\text{Ph}$ ) [1b]. Subsequently, some related compounds such as  $\{\text{MoCpCl}[(\text{CH}_2)_n(2\text{-C}_6\text{H}_4\text{N})_2]\}$  and  $\{\text{Mo}(\text{OBU}^i)_2[(\text{CH}_2)_n(2\text{-C}_6\text{H}_4\text{N})_2]\}$  ( $n = 1, 2$ ) were prepared [2]. The synthesis and reactivity of the  $\text{d}^0$   $[\text{Mo}(\text{NAr})_3]$  core ( $\text{Ar} = 2,6\text{-Pr}_2^i\text{C}_6\text{H}_3$ ) has been exten-

sively studied by Morrison and Wigley [3]. We have now extended our studies to the monoalkyl complexes  $[\text{MoCl}(\text{NAr})_2(\text{R})]$  ( $\text{R} = \text{CH}_2\text{CMe}_2\text{Ph}$  and  $\text{CH}_2\text{CMe}_3$ ) and describe a number of derivatives made by replacing Cl with carbon, oxygen and nitrogen ligands.

## 2. Results and discussion

Interaction of  $[\text{MoCl}_2(\text{NAr})_2(\text{dme})]$  ( $\text{Ar} = 2,6\text{-Pr}_2^i\text{C}_6\text{H}_3$ ) with one equivalent of Grignard reagent  $\text{RMgCl}$  in diethyl ether at  $-78^\circ\text{C}$  affords, after work-up, multigram quantities of the monoalkyl complexes  $[\text{MoCl}(\text{NAr})_2\text{R}]$  ( $\text{R} = \text{CH}_2\text{CMe}_2\text{Ph}$  (**1**) or  $\text{CH}_2\text{CMe}_3$  (**2**)) as orange-red crystalline solids. The compounds doubtless have the same basic structure; the molecular structure of **1**, determined by X-ray crystallography, is shown in Fig. 1, and selected bond lengths and angles are given in Table 1.

\* Corresponding author. Tel.: +44-1603-593137; fax: +44-1603-592003.

E-mail address: Carl.Redshaw@uea.ac.uk (C. Redshaw).

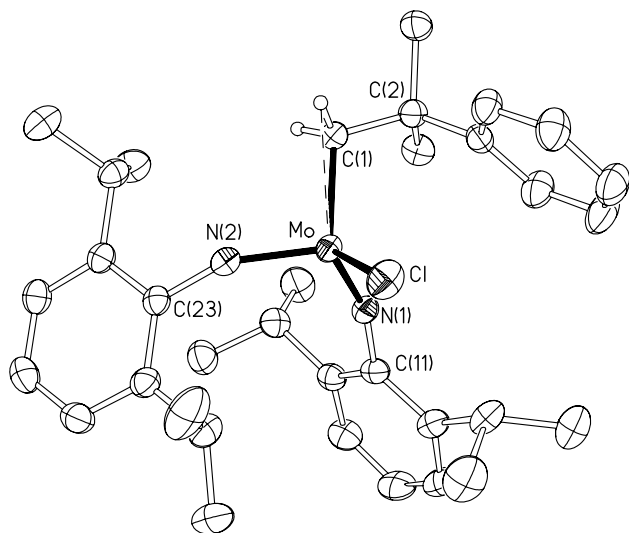


Fig. 1. Molecular structure of **1**, without most H atoms and minor disorder components, and with key atoms labeled. Displacement ellipsoids here and in other figures are drawn at the 50% probability level.

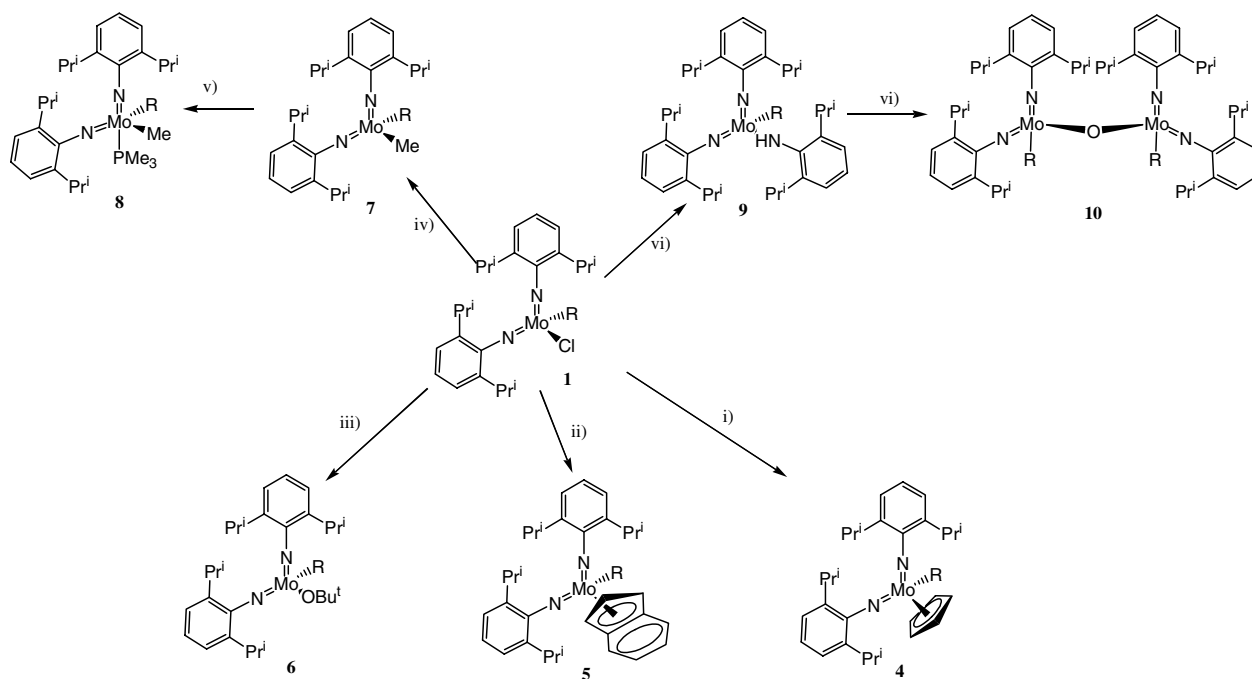
The coordination geometry about the metal centre is best described as distorted tetrahedral with angles in the range 99.91(7)–122.67(5)°. The two *cis* imido groups are similar; the Mo–N distances are essentially equal, 1.7364(15) and 1.7435(15) Å, with Mo–N–C angles of 161.59(13)° and 152.94(12)°, respectively. The latter is considered to be at the lower limit regarded as a ‘linear’ imido group acting as a four-electron donor [4]. An interesting feature is the presence of an  $\alpha$ -agostic interaction involving a hydrogen atom H(1A) on the neophyl methylene carbon. The metal–hydrogen distance (resulting from free refinement) is 2.46(2) Å with an Mo–C(1)–H(1A) angle of 100.0(13)°, comparable with the two  $\alpha$ -agostic interactions found in the related mixed-imido complex [Mo(NAr)(NBu<sup>t</sup>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>] [**1**].

The mixed-imido complex [MoCl(NAr)(NBu<sup>t</sup>)(CH<sub>2</sub>CMe<sub>2</sub>Ph)] (**3**) is similarly formed from [MoCl<sub>2</sub>(NAr)(NBu<sup>t</sup>)(dme)] and neophyl Grignard in diethyl ether.

The mono-neophyl complex **1** is a useful starting material for the synthesis of four- and five-coordinate

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

Mo–Cl	2.3295(5)	Mo–C(1)	2.1296(18)
Mo–N(1)	1.7364(15)	Mo–N(2)	1.7435(15)
N(1)–C(11)	1.401(2)	N(2)–C(23)	1.399(2)
Cl–Mo–C(1)	122.67(5)	Cl–Mo–N(1)	111.53(5)
Cl–Mo–N(2)	108.24(5)	C(1)–Mo–N(1)	105.07(7)
C(1)–Mo–N(2)	99.91(7)	N(1)–Mo–N(2)	108.21(7)
Mo–C(1)–C(2)	115.55(12)	Mo–N(1)–C(11)	161.59(13)
Mo–N(2)–C(23)	152.94(12)		



Scheme 1. Reagents and conditions. (i) LiCp, –78 °C, Et<sub>2</sub>O, 24 h; (ii) Li(Indenyl), –78 °C, Et<sub>2</sub>O, 24 h; (iii) LiOBu<sup>t</sup>, –78 °C, Et<sub>2</sub>O, 12 h; (iv) MeMgI, 78 °C, Et<sub>2</sub>O, 12 h; (v) PMe<sub>3</sub>, –198 °C, pentane; (vi) LiNHAr, Et<sub>2</sub>O, 1 h; (vii) [dried in vacuo, 50 °C, 12 h; Et<sub>2</sub>O, 48 h, 25 °C] × 3.

Table 2  
<sup>1</sup>H NMR data (benzene-d<sub>6</sub>, <sup>a</sup> CDCl<sub>3</sub>, <sup>b</sup> 298 K)

Compound	Shift	Rel. integration	Multiplicity	<i>J</i> (Hz)	Assignment
<b>1<sup>a</sup></b>	7.43	2	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 8.5	<i>o</i> -C <sub>6</sub> H <sub>5</sub>
	7.24	2	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.7	<i>m</i> -C <sub>6</sub> H <sub>5</sub>
	7.12	1	d	*	<i>p</i> -C <sub>6</sub> H <sub>5</sub>
	6.92–6.85	5	m		<i>o, m, p</i> -C <sub>6</sub> H <sub>5</sub>
	3.59	4	sept	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.9	CHMe <sub>2</sub>
	3.01	2	s		CH <sub>2</sub> CMe <sub>2</sub> Ph
	1.57	6	s		CH <sub>2</sub> CMe <sub>2</sub> Ph
	1.08	24	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.1	CHMe <sub>2</sub>
<b>2<sup>a</sup></b>	6.96–6.88	6	m		<i>m, p</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	3.67	4	sept	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.9	CHMe <sub>2</sub>
	2.79	2	s		CH <sub>2</sub> CMe <sub>3</sub>
	1.23	6	s		CH <sub>2</sub> CMe <sub>3</sub>
	1.13	12	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.9	CHMe <sub>2</sub>
	1.09	12	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.9	CHMe <sub>2</sub>
<b>3<sup>a</sup></b>	7.39	2	dd	<sup>3</sup> <i>J</i> <sub>HH</sub> 8.0 <sup>4</sup> <i>J</i> <sub>HH</sub> 0.8	<i>o</i> -C <sub>6</sub> H <sub>5</sub>
	7.22	2	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.7	<i>m</i> -C <sub>6</sub> H <sub>5</sub>
	7.09	2	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.3	<i>p</i> -C <sub>6</sub> H <sub>5</sub>
	7.04–6.90	3	m		<i>m, p</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	3.58	2	sept	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
	3.18	1	d	<sup>2</sup> <i>J</i> <sub>HH</sub> 13.5	CH <sub>2</sub> CMe <sub>2</sub> Ph
	2.37	1	d	<sup>2</sup> <i>J</i> <sub>HH</sub> 13.5	CH <sub>2</sub> CMe <sub>2</sub> Ph
	1.58	3	s		CH <sub>2</sub> CMe <sub>2</sub> Ph
	1.54	3	s		CH <sub>2</sub> CMe <sub>2</sub> Ph
	1.28	6	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
	1.23	6	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
	1.00	9	s		NCMe <sub>3</sub>
<b>4<sup>b</sup></b>	7.62	2	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.6	<i>o</i> -C <sub>6</sub> H <sub>5</sub>
	7.46	2	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.7	<i>m</i> -C <sub>6</sub> H <sub>5</sub>
	7.32	1	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.2	<i>p</i> -C <sub>6</sub> H <sub>5</sub>
	7.02	4	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.7	<i>m</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	6.95–6.91	2	m		<i>p</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	5.77	5	s		C <sub>5</sub> H <sub>5</sub>
	3.54	4	sept	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.9	CHMe <sub>2</sub>
	3.02	2	s		CH <sub>2</sub> CMe <sub>2</sub> Ph
	1.42	6	s		CH <sub>2</sub> CMe <sub>2</sub> Ph
	1.14	12	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.9	CHMe <sub>2</sub>
	<b>5<sup>b</sup></b>	7.79	2	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.8
7.59		2	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.7	<i>m</i> -C <sub>6</sub> H <sub>5</sub>
7.40		1	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.3	<i>p</i> -C <sub>6</sub> H <sub>5</sub>
7.06		2	m		H <sub>5,6</sub> -C <sub>9</sub> H <sub>7</sub>
6.96–6.82		8	m		<i>m, p</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub> H <sub>4,7</sub> -C <sub>9</sub> H <sub>7</sub>
6.10		2	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 3.0	H <sub>1,3</sub> -C <sub>9</sub> H <sub>7</sub>
5.93		1	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 3.3	H <sub>2</sub> -C <sub>9</sub> H <sub>7</sub>
3.19		4	br. sept		CHMe <sub>2</sub>
2.66		2	s		CH <sub>2</sub> CMe <sub>2</sub> Ph
1.49		6	s		CH <sub>2</sub> CMe <sub>2</sub> Ph
1.06		24	pseudo t	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.5	CHMe <sub>2</sub>
<b>6<sup>a</sup></b>	7.53	2	dd	<sup>3</sup> <i>J</i> <sub>HH</sub> 8.1 <sup>4</sup> <i>J</i> <sub>HH</sub> 1.1	<i>o</i> -C <sub>6</sub> H <sub>5</sub>
	7.21	2	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.8	<i>m</i> -C <sub>6</sub> H <sub>5</sub>
	7.08–6.90	7	m		<i>m, p</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	3.73	4	sept	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.9	CHMe <sub>2</sub>
	3.06	2	s		CH <sub>2</sub> CMe <sub>2</sub> Ph
	1.68	6	s		CH <sub>2</sub> CMe <sub>2</sub> Ph
	1.29	9	s		OCMe <sub>3</sub>
	1.14	24	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.9	CHMe <sub>2</sub>

Table 2 (continued)

Compound	Shift	Rel. integration	Multiplicity	<i>J</i> (Hz)	Assignment
<b>7<sup>b</sup></b>	7.65	2	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.5	<i>o</i> -C <sub>6</sub> H <sub>5</sub>
	7.43	2	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.3	<i>m</i> -C <sub>6</sub> H <sub>5</sub>
	7.34	1	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.1	<i>p</i> -C <sub>6</sub> H <sub>5</sub>
	7.10–6.95	6	m		<i>m,p</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	3.47	4	sept	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
	2.48	2	s		CH <sub>2</sub> CM <sub>2</sub> Ph
	1.65	6	s		CH <sub>2</sub> CM <sub>2</sub> Ph
	1.11	12	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
	1.08	12	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
	0.37	3	s		CH <sub>3</sub>
<b>8<sup>a</sup></b>	7.51	2	dd	<sup>3</sup> <i>J</i> <sub>HH</sub> 8.4 <sup>4</sup> <i>J</i> <sub>HH</sub> 1.2	<i>o</i> -C <sub>6</sub> H <sub>5</sub>
	7.18	2	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.3	<i>m</i> -C <sub>6</sub> H <sub>5</sub>
	7.04–6.95	7	m		<i>p</i> -C <sub>6</sub> H <sub>5</sub> <i>m,p</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	3.89	4	sept	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
	2.53	2	s		CH <sub>2</sub> CM <sub>2</sub> Ph
	1.51	6	s		CH <sub>2</sub> CM <sub>2</sub> Ph
	1.24	12	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
	1.17	12	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
	0.91	3	s		CH <sub>3</sub>
	0.79	9	d	<sup>3</sup> <i>J</i> <sub>HP</sub> 4.5	PMe <sub>3</sub>
<b>9<sup>b</sup></b>	7.61	2	s		<i>o</i> -C <sub>6</sub> H <sub>5</sub>
	7.32	2	t		<i>m</i> -C <sub>6</sub> H <sub>5</sub>
	7.20–6.80	11	m		<i>p</i> -C <sub>6</sub> H <sub>5</sub> NHAr C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub> NHAr NAr
	3.46	2	t		CHMe <sub>2</sub>
	3.40	4	sept	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
	2.81	2	s		CH <sub>2</sub> CM <sub>2</sub> Ph
	1.65	6	s		CH <sub>2</sub> CM <sub>2</sub> Ph
	1.32	12	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
	1.26	12	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
	<b>10<sup>a</sup></b>	7.58	2	dd	<sup>3</sup> <i>J</i> <sub>HH</sub> 8.4 <sup>4</sup> <i>J</i> <sub>HH</sub> 1.0
7.21		2	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.3	<i>m</i> -C <sub>6</sub> H <sub>5</sub>
7.04		1	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.4	<i>p</i> -C <sub>6</sub> H <sub>5</sub>
6.92–6.85		6	m		<i>m,p</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
3.71		4	sept	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
3.29		2	s		CH <sub>2</sub> CM <sub>2</sub> Ph
1.86		6	s		CH <sub>2</sub> CM <sub>2</sub> Ph
1.15		12	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
1.07		12	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
<b>11<sup>b</sup></b>		7.49	2	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 8.4
	7.30	2	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.7	<i>m</i> -C <sub>6</sub> H <sub>5</sub>
	7.15	1	t	<sup>3</sup> <i>J</i> <sub>HH</sub> 7.5	<i>p</i> -C <sub>6</sub> H <sub>5</sub>
	7.10–6.80	7	m		NH <sup><i>t</i></sup> Bu <i>m,p</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	3.48	4	sept	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.8	CHMe <sub>2</sub>
	2.55	2	s		CH <sub>2</sub> CM <sub>2</sub> Ph
	1.55	6	s		CH <sub>2</sub> CM <sub>2</sub> Ph
	1.18	9	s		NCMe <sub>3</sub>
	1.07	12	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.9	CHMe <sub>2</sub>
	1.04	12	d	<sup>3</sup> <i>J</i> <sub>HH</sub> 6.9	CHMe <sub>2</sub>

s, Singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; br, broad; \*, obscured.

Table 3  
 $^{13}\text{C}$  NMR data (benzene- $\text{d}_6$ ,<sup>a</sup>  $\text{CdCl}_3$ ,<sup>b</sup> 298 K)

Compound	Shift	Multiplicity	$J$ (Hz)	Assignment	
<b>1<sup>a</sup></b>	153.17	m		<i>o</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$	
	148.31	m		<i>ipso</i> - $\text{C}_6\text{H}_5$	
	143.31s			<i>ipso</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$	
	129.30	dd	$^1J_{\text{CH}}$ 160.2 $^2J_{\text{CH}}$ 8.1	<i>p</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$	
	127.49	m	*	<i>m</i> - $\text{C}_6\text{H}_5$	
	127.19	dt	*	<i>p</i> - $\text{C}_6\text{H}_5$	
	126.33	dt	$^1J_{\text{CH}}$ 157.74	<i>o</i> - $\text{C}_6\text{H}_5$	
	123.02	m	$^1J_{\text{CH}}$ 159.3	<i>m</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$	
	73.87	th	$^1J_{\text{CH}}$ 126.4 $^3J_{\text{CH}}$ 4.8	$\text{CH}_2\text{CMe}_2\text{Ph}$	
	39.58	s		$\text{CH}_2\text{CMe}_2\text{Ph}$	
	31.99	qq	$^1J_{\text{CH}}$ 126.0 $^3J_{\text{CH}}$ 4.4	$\text{CH}_2\text{CMe}_2\text{Ph}$	
	28.70	d	$^1J_{\text{CH}}$ 128.3	$\text{CHMe}_2$	
	23.70	qt	$^1J_{\text{CH}}$ 126.2 $^3J_{\text{CH}}$ 5.0	$\text{CHMe}_2$	
	23.54	qt	$^1J_{\text{CH}}$ 126.2 $^3J_{\text{CH}}$ 5.0	$\text{CHMe}_2$	
	<b>2<sup>a</sup></b>	155.22	s		<i>ipso</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
		143.22	s		<i>o</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
		127.58	d	*	<i>p</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
123.05		d	$^1J_{\text{CH}}$ 157.8	<i>m</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$	
77.51		t	$^1J_{\text{CH}}$ 120.7	$\text{CH}_2\text{CMe}_3$	
33.53		s		$\text{CH}_2\text{CMe}_3$	
32.62		q	$^1J_{\text{CH}}$ 124.2	$\text{CH}_2\text{CMe}_3$	
28.93		d	$^1J_{\text{CH}}$ 127.5	$\text{CHCMe}_2$	
23.49		q	$^1J_{\text{CH}}$ 127.9	$\text{CHCMe}_2$	
<b>3<sup>a</sup></b>		153.69	s		<i>ipso</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
	149.96	s		<i>ipso</i> - $\text{C}_6\text{H}_5$	
	141.79	s		<i>o</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$	
	128.94	dd	$^1J_{\text{CH}}$ * $^2J_{\text{CH}}$ 7.6	<i>o</i> - $\text{C}_6\text{H}_5$	
	126.67	d	$^1J_{\text{CH}}$ 160.1	<i>p</i> - $\text{C}_6\text{H}_5$	
	126.49	dt	$^1J_{\text{CH}}$ 160.4 $^2J_{\text{CH}}$ 7.5	<i>p</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$	
	126.01	dt	$^1J_{\text{CH}}$ 159.9	<i>m</i> - $\text{C}_6\text{H}_5$	
	122.93	m	$^1J_{\text{CH}}$ 157.1	<i>m</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$	
	73.41	s		$\text{NCMe}_3$	
	71.16	t	$^1J_{\text{CH}}$ 125.6	$\text{CH}_2\text{CMe}_2\text{Ph}$	
	39.41	s		$\text{CH}_2\text{CMe}_2\text{Ph}$	
	32.57	q	$^1J_{\text{CH}}$ 126.3	$\text{CH}_2\text{CMe}_2\text{Ph}$	
	32.04	q	$^1J_{\text{CH}}$ 126.2	$\text{CH}_2\text{CMe}_2\text{Ph}$	
	30.98	q	$^1J_{\text{CH}}$ 127.4	$\text{NCMe}_3$	
	28.81	d	$^1J_{\text{CH}}$ 128.2	$\text{CHMe}_2$	
	23.76	q	$^1J_{\text{CH}}$ 125.9	$\text{CHMe}_2$	
	23.33	q	$^1J_{\text{CH}}$ 125.9	$\text{CHMe}_2$	
<b>4<sup>b</sup></b>	153.60	s		<i>ipso</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$	
	152.56	s		<i>ipso</i> - $\text{C}_6\text{H}_5$	
	140.98	s		<i>o</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$	
	128.20	dd	$^1J_{\text{CH}}$ 160.0 $^2J_{\text{CH}}$ 7.7	<i>o</i> - $\text{C}_6\text{H}_5$	
	126.04	dt	$^1J_{\text{CH}}$ 156.5 $^2J_{\text{CH}}$ 6.9	<i>p</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$	
	125.73	dt	$^1J_{\text{CH}}$ 160.8 $^2J_{\text{CH}}$ 7.4	<i>p</i> - $\text{C}_6\text{H}_5$	
	123.74	d	$^1J_{\text{CH}}$ 159.8	<i>m</i> - $\text{C}_6\text{H}_5$	
	122.38	ddd	$^1J_{\text{CH}}$ 155.1 $^2J_{\text{CH}}$ 7.2 $^3J_{\text{CH}}$ 5.1	<i>m</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$	
	105.91	m	$^1J_{\text{CH}}$ 175.2	$\text{C}_5\text{H}_5$	
	47.60	t	$^1J_{\text{CH}}$ 126.3	$\text{CH}_2\text{CMe}_2\text{Ph}$	
	41.80	s		$\text{CH}_2\text{CMe}_2\text{Ph}$	

Table 3 (continued)

Compound	Shift	Multiplicity	$J$ (Hz)	Assignment
<b>5<sup>b</sup></b>	34.16	q	$^1J_{\text{CH}}$ 126.0	$\text{CH}_2\text{CMe}_2\text{Ph}$
	27.68	d	$^1J_{\text{CH}}$ 126.3	$\text{CHMe}_2$
	23.88	q	$^1J_{\text{CH}}$ 126.3	$\text{CHMe}_2$
	23.83	q	$^1J_{\text{CH}}$ 126.3	$\text{CHMe}_2$
	153.17	s		<i>ipso</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
	152.64	s		<i>ipso</i> - $\text{C}_6\text{H}_5$
	141.00	s		<i>o</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
	128.26	m	*	<i>o</i> - $\text{C}_6\text{H}_5$
	127.68	s		<i>ipso</i> - $\text{C}_9\text{H}_7$
	126.60	m	*	<i>m</i> - $\text{C}_6\text{H}_5$
	125.96	dt	$^1J_{\text{CH}}$ 162.4 $^2J_{\text{CH}}$ 7.0	<i>p</i> - $\text{C}_6\text{H}_5$
	125.61	dd	$^1J_{\text{CH}}$ 160.4 $^2J_{\text{CH}}$ 7.6	$\text{C}_{4,7}$ - $\text{C}_9\text{H}_7$
	123.88	m	$^1J_{\text{CH}}$ 159.6	<i>p</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
	122.06	m	$^1J_{\text{CH}}$ 155.5	<i>m</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
	121.31	dd	$^1J_{\text{CH}}$ 164.4 $^2J_{\text{CH}}$ 4.9	$\text{C}_{5,6}$ - $\text{C}_9\text{H}_7$
	110.44	dt	$^1J_{\text{CH}}$ 171.7 $^2J_{\text{CH}}$ 4.2	$\text{C}_2$ - $\text{C}_9\text{H}_7$
	89.94	Br. d	$^1J_{\text{CH}}$ 172.5	$\text{C}_{1,3}$ - $\text{C}_9\text{H}_7$
	51.29	t	$^1J_{\text{CH}}$ 126.3	$\text{CH}_2\text{CMe}_2\text{Ph}$
	41.32	s		$\text{CH}_2\text{CMe}_2\text{Ph}$
	<b>6<sup>a</sup></b>	34.58	q	$^1J_{\text{CH}}$ 126.0
27.63		d	$^1J_{\text{CH}}$ 128.3	$\text{CHMe}_2$
24.56		qt	$^1J_{\text{CH}}$ 125.7	$\text{CHMe}_2$
22.90		qt	$^1J_{\text{CH}}$ 125.5	$\text{CHMe}_2$
153.47		s		<i>ipso</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
152.37		s		<i>ipso</i> - $\text{C}_6\text{H}_5$
142.28		s		<i>o</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
128.49		dd	$^2J_{\text{CH}}$ 16.2	<i>o</i> - $\text{C}_6\text{H}_5$
125.87		m	*	<i>p</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
125.79		m	*	<i>p</i> - $\text{C}_6\text{H}_5$
125.75		d	$^1J_{\text{CH}}$ 160.1	<i>m</i> - $\text{C}_6\text{H}_5$
122.84		m	$^1J_{\text{CH}}$ 155.9	<i>m</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
81.84		s		$\text{OC}(\text{CH}_3)_3$
63.68		t	$^1J_{\text{CH}}$ 125.6	$\text{CH}_2\text{CMe}_2\text{Ph}$
39.71		s		$\text{CH}_2\text{CMe}_2\text{Ph}$
32.62		q	$^1J_{\text{CH}}$ 125.9	$\text{CH}_2\text{CMe}_2\text{Ph}$
32.32		q	$^1J_{\text{CH}}$ 125.9	$\text{OC}(\text{CH}_3)_3$
28.60		d	$^1J_{\text{CH}}$ 128.0	$\text{CHMe}_2$
23.74		q	$^1J_{\text{CH}}$ 125.5	$\text{CHMe}_2$
<b>7<sup>b</sup></b>		152.73	s	
	148.52	s		<i>ipso</i> - $\text{C}_6\text{H}_5$
	142.33	s		<i>o</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
	128.98	dd	$^1J_{\text{CH}}$ * $^2J_{\text{CH}}$ 7.4	<i>o</i> - $\text{C}_6\text{H}_5$
	126.84	dt	$^1J_{\text{CH}}$ 160.8 $^2J_{\text{CH}}$ 7.1	<i>p</i> - $\text{C}_6\text{H}_5$
	126.25	dt	$^1J_{\text{CH}}$ * $^2J_{\text{CH}}$ 5.9	<i>p</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
	125.24	d	$^1J_{\text{CH}}$ 159.2	<i>m</i> - $\text{C}_6\text{H}_5$
	122.32	d	$^1J_{\text{CH}}$ 155.3	<i>m</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
	72.03	t	$^1J_{\text{CH}}$ 123.4	$\text{CH}_2\text{CMe}_2\text{Ph}$
	38.70	s		$\text{CH}_2\text{CMe}_2\text{Ph}$
	34.86	q	$^1J_{\text{CH}}$ 126.8	$\text{CH}_3$
	32.75	m	$^1J_{\text{CH}}$ 128.8	$\text{CH}_2\text{CMe}_2\text{Ph}$
<b>8<sup>a</sup></b>	28.13	d	$^1J_{\text{CH}}$ 128.4	$\text{CHMe}_2$
	23.47	q	$^1J_{\text{CH}}$ 126.3	$\text{CHMe}_2$
	23.13	q	$^1J_{\text{CH}}$ 125.0	$\text{CHMe}_2$
	153.46	s		<i>ipso</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
	153.19	s		<i>ipso</i> - $\text{C}_6\text{H}_5$
	143.36	s		<i>o</i> - $\text{C}_6\text{H}_3^i\text{Pr}_2$
	128.78	dd	$^2J_{\text{CH}}$ 6.1	<i>o</i> - $\text{C}_6\text{H}_5$

Table 3 (continued)

Compound	Shift	Multiplicity	<i>J</i> (Hz)	Assignment
<b>9<sup>b</sup></b>	125.98	m	*	<i>p</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	125.91	d	*	<i>p</i> -C <sub>6</sub> H <sub>5</sub>
	125.43	d	<sup>1</sup> <i>J</i> <sub>CH</sub> 159.2	<i>m</i> -C <sub>6</sub> H <sub>5</sub>
	122.90	m	<sup>1</sup> <i>J</i> <sub>CH</sub> 159.7	<i>m</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	59.19	t	<sup>1</sup> <i>J</i> <sub>CH</sub> 125.9	CH <sub>2</sub> CMe <sub>2</sub> Ph
	41.09	s		CH <sub>2</sub> CMe <sub>2</sub> Ph
	33.13	m	<sup>1</sup> <i>J</i> <sub>CH</sub> 123.6	CH <sub>2</sub> CMe <sub>2</sub> Ph
	28.18	d	<sup>1</sup> <i>J</i> <sub>CH</sub> 126.2	CHMe <sub>2</sub>
	24.70	q	<sup>1</sup> <i>J</i> <sub>CH</sub> 125.9	CHMe <sub>2</sub>
	23.98	q	<sup>1</sup> <i>J</i> <sub>CH</sub> 125.8	CH <sub>3</sub>
	23.55	q	<sup>1</sup> <i>J</i> <sub>CH</sub> 125.8	CHMe <sub>2</sub>
	14.74	dq	<sup>2</sup> <i>J</i> <sub>CP</sub> 5.2	PMe <sub>3</sub>
	152.54	s		<i>ipso</i> -NHC <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	148.63	s		<i>ipso</i> -NC <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	142.41	s		<i>o</i> -NC <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	138.99	s		<i>o</i> -NHC <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	125.13	d	<sup>1</sup> <i>J</i> <sub>CH</sub> 159.9	<i>p</i> -NC <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	123.38	d	<sup>1</sup> <i>J</i> <sub>CH</sub> 160.1	<i>p</i> -NHC <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	122.92	m	*	<i>m</i> -NHC <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	122.31	m	*	<i>m</i> -NC <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	66.57	t	<sup>1</sup> <i>J</i> <sub>CH</sub> 121.8	CH <sub>2</sub> CMe <sub>2</sub> Ph
	39.84	s		CH <sub>2</sub> CMe <sub>2</sub> Ph
	32.18	q	<sup>1</sup> <i>J</i> <sub>CH</sub> 126.5	CH <sub>2</sub> CMe <sub>2</sub> Ph
	28.28	d	<sup>1</sup> <i>J</i> <sub>CH</sub> 127.4	CHMe <sub>2</sub>
	24.05	q	<sup>1</sup> <i>J</i> <sub>CH</sub> 125.9	CHMe <sub>2</sub>
	23.61	q	<sup>1</sup> <i>J</i> <sub>CH</sub> 125.8	CHMe <sub>2</sub>
	23.23	q	<sup>1</sup> <i>J</i> <sub>CH</sub> 125.9	CHMe <sub>2</sub>
<b>10<sup>a</sup></b>	153.69	s		<i>ipso</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	153.01	s		<i>ipso</i> -C <sub>6</sub> H <sub>5</sub>
	142.52	s		<i>o</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	128.59	dd	<sup>1</sup> <i>J</i> <sub>CH</sub> *	<i>o</i> -C <sub>6</sub> H <sub>5</sub>
			<sup>2</sup> <i>J</i> <sub>CH</sub> 7.6	
	126.40	d	<sup>1</sup> <i>J</i> <sub>CH</sub> 159.9	<i>p</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	125.96	dt	<sup>1</sup> <i>J</i> <sub>CH</sub> 161.2	<i>p</i> -C <sub>6</sub> H <sub>5</sub>
			<sup>2</sup> <i>J</i> <sub>CH</sub> 7.6	
	125.49	dt	<sup>1</sup> <i>J</i> <sub>CH</sub> 154.3	<i>m</i> -C <sub>6</sub> H <sub>5</sub>
			<sup>2</sup> <i>J</i> <sub>CH</sub> 6.9	
	122.86	m	<sup>1</sup> <i>J</i> <sub>CH</sub> 156.3	<i>m</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
68.54	t	<sup>1</sup> <i>J</i> <sub>CH</sub> 124.3	CH <sub>2</sub> CMe <sub>2</sub> Ph	
39.88	s		CH <sub>2</sub> CMe <sub>2</sub> Ph	
31.83	q	<sup>1</sup> <i>J</i> <sub>CH</sub> 128.6	CH <sub>2</sub> CMe <sub>2</sub> Ph	
28.78	d	<sup>1</sup> <i>J</i> <sub>CH</sub> 127.6	C HMe <sub>2</sub>	
23.78	qt	<sup>1</sup> <i>J</i> <sub>CH</sub> 125.9	CHMe <sub>2</sub>	
23.51	qt	<sup>1</sup> <i>J</i> <sub>CH</sub> 125.7	CHMe <sub>2</sub>	
<b>11<sup>b</sup></b>	152.96	s		<i>ipso</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	152.62	s		<i>ipso</i> -C <sub>6</sub> H <sub>5</sub>
	141.59	s		<i>o</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	128.00	m	<sup>1</sup> <i>J</i> <sub>CH</sub> 149.0	<i>m</i> -C <sub>6</sub> H <sub>5</sub>
	126.02	dt	<sup>1</sup> <i>J</i> <sub>CH</sub> 156.2	<i>p</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
			<sup>2</sup> <i>J</i> <sub>CH</sub> 7.0	
	125.25	dt	<sup>1</sup> <i>J</i> <sub>CH</sub> 159.9	<i>p</i> -C <sub>6</sub> H <sub>5</sub>
			<sup>2</sup> <i>J</i> <sub>CH</sub> 7.3	
	124.40	d	<sup>1</sup> <i>J</i> <sub>CH</sub> 159.4	<i>o</i> -C <sub>6</sub> H <sub>5</sub>
	122.26	m	<sup>1</sup> <i>J</i> <sub>CH</sub> 156.8	<i>m</i> -C <sub>6</sub> H <sub>3</sub> <sup><i>i</i></sup> Pr <sub>2</sub>
	61.55	s		NCMe <sub>3</sub>
	57.78	t	<sup>1</sup> <i>J</i> <sub>CH</sub> 120.9	CH <sub>2</sub> CMe <sub>2</sub> Ph
	39.91	s		CH <sub>2</sub> CMe <sub>2</sub> Ph
	33.18	q	<sup>1</sup> <i>J</i> <sub>CH</sub> 125.8	NCMe <sub>3</sub>
	32.80	q	<sup>1</sup> <i>J</i> <sub>CH</sub> 126.5	CH <sub>2</sub> CMe <sub>2</sub> Ph
	28.29	d	<sup>1</sup> <i>J</i> <sub>CH</sub> 127.4	CHMe <sub>2</sub>
	23.42	m	<sup>1</sup> <i>J</i> <sub>CH</sub> 125.8	CHMe <sub>2</sub>
23.09	m	<sup>1</sup> <i>J</i> <sub>CH</sub> 125.9	CHMe <sub>2</sub>	

s, Singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; br, broad; \*, obscured.

bis(imido) complexes of molybdenum(VI); see Scheme 1. NMR data ( $^1\text{H}$  and  $^{13}\text{C}$ ) of complexes **1** through **11** are presented in Tables 2 and 3.

Interaction of **1** with LiCp (Cp = cyclopentadienyl) or LiInd (Ind = Indenyl) in diethyl ether at  $-78\text{ }^\circ\text{C}$  gives the compounds  $[\text{MoR}'(\text{NAr})_2(\text{CH}_2\text{CMe}_2\text{Ph})]$  ( $\text{R}' = \text{Cp}$  (**4**) or Ind (**5**)), respectively, in high yields. These compounds are very soluble in hydrocarbons and can be crystallized from pentane at  $-40\text{ }^\circ\text{C}$ . The molecular structure of **4** is shown in Fig. 2, with selected bond lengths and angles in Table 4. The molecule has a distorted tetrahedral geometry with an approximate (i.e. non-crystallographic) mirror plane of symmetry containing the metal and the methylene C(1) atom of the neophyl group and bisecting the Cp ligand.

The angles around the molybdenum centre vary from  $95.85(6)^\circ$  to  $106.33(7)^\circ$ , excluding the angles involving the Cp ring carbon atoms. The Mo–C (Cp) bond lengths range from 2.3927(18) to 2.5081(18) Å, indicating a slight tilting away from the sterically bulky neophyl group. As in **1**, the two imido groups are similar: Mo–N 1.7610(15) and 1.7693(14) Å, Mo–N–C  $163.99(14)^\circ$  and

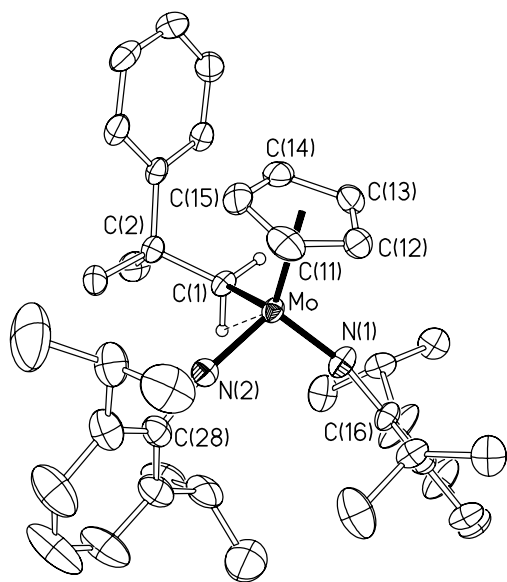


Fig. 2. Molecular structure of **4**, without most H atoms and minor disorder components, and with key atoms labelled.

$171.11(14)^\circ$ . Interestingly, there is also a similar  $\alpha$ -agostic interaction involving H(1B) and the metal centre: Mo–H(1B) = 2.56(2) Å, Mo–C(1)–H(1B) =  $99.0(11)^\circ$ . The related compound  $[\text{CpMo}(\text{NAr})_2(\text{NHAr})]$  has been reported previously [3].

The structure of the compound  $[\text{MoInd}(\text{NAr})_2(\text{CH}_2\text{CMe}_2\text{Ph})]$  (**5**) is shown in Fig. 3; selected bond lengths and angles are given in Table 5. As previously observed in compounds **1** and **4**, the geometry about the molybdenum centre is distorted tetrahedral with near-linear *cis* arylimido ligands (Mo–N–C =  $157.41(14)^\circ$  and  $169.35(16)^\circ$ ). The bonding of the indenyl ring, for which the Mo–C distances differ significantly, in the range 2.350(2)–2.641(2) Å, is best described as slipped, i.e.  $\eta^3$ . The indenyl ring also displays a slight puckering; the greatest deviations from the mean plane of the ring atoms are for C(36) ( $-0.0451\text{ Å}$ ) and C(37) ( $+0.0450\text{ Å}$ ) (+ denotes closer to the metal). There is no clear evidence of  $\alpha$ -agostic bonding in **5** (Mo–H(1A) = 2.61(3) Å, Mo–H(1B) = 2.58(3) Å). We note that Sundermeyer and coworkers [5] have recently reported a number of bis(imido) indenyl complexes of molybdenum.

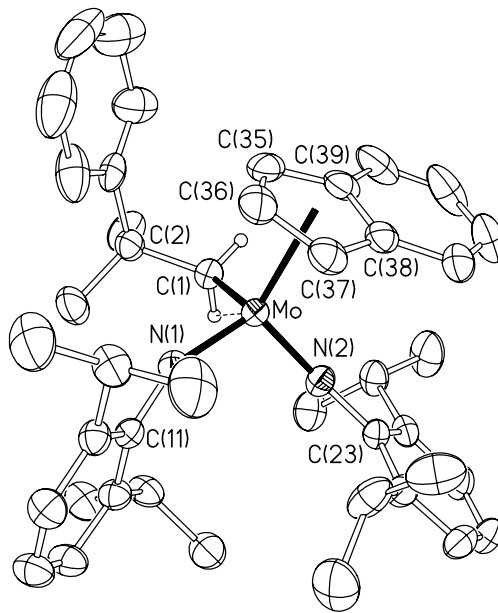


Fig. 3. Molecular structure of **5**, without most H atoms, and with key atoms labelled.

Table 4  
Selected bond lengths (Å) and angles ( $^\circ$ ) for **4**

Mo–C(1)	2.2103(17)	Mo–C(11)	2.3927(18)
Mo–C(12)	2.4101(18)	Mo–C(13)	2.4983(18)
Mo–C(14)	2.5081(18)	Mo–C(15)	2.4690(18)
Mo–N(1)	1.7693(14)	Mo–N(2)	1.7610(15)
N(1)–C(16)	1.385(2)	N(2)–C(28)	1.392(2)
C(1)–Mo–N(1)	95.85(6)	C(1)–Mo–N(2)	95.91(7)
N(1)–Mo–N(2)	106.33(7)	Mo–C(1)–C(2)	126.49(12)
Mo–N(1)–C(16)	163.99(14)	Mo–N(2)–C(28)	171.11(14)



Table 5  
Selected bond lengths (Å) and angles (°) for **5**

Mo–C(1)	2.209(2)	Mo–N(1)	1.7674(16)
Mo–N(2)	1.7568(15)	Mo–C(35)	2.496(2)
Mo–C(36)	2.397(2)	Mo–C(37)	2.350(2)
Mo–C(38)	2.594(2)	Mo–C(39)	2.641(2)
C(1)–Mo–N(1)	101.36(8)	C(1)–Mo–N(2)	98.76(8)
N(1)–Mo–N(2)	106.90(8)	Mo–C(1)–C(2)	125.87(14)
Mo–N(1)–C(11)	157.41(14)	Mo–N(2)–C(23)	169.35(16)

The chloro ligands of **1** can be cleanly replaced by treatment with LiOBu<sup>t</sup> to give the corresponding four-coordinate species [Mo(OBu<sup>t</sup>)(NAr)<sub>2</sub>(CH<sub>2</sub>CMe<sub>2</sub>Ph)] (**6**), and with MeMgBr to give [MoMe(NAr)<sub>2</sub>(CH<sub>2</sub>CMe<sub>2</sub>Ph)] (**7**). In the presence of PMe<sub>3</sub>, the latter reaction gives a five-coordinate adduct [MoMe(PMe<sub>3</sub>)(NAr)<sub>2</sub>(CH<sub>2</sub>CMe<sub>2</sub>Ph)] (**8**), the NMR data of which

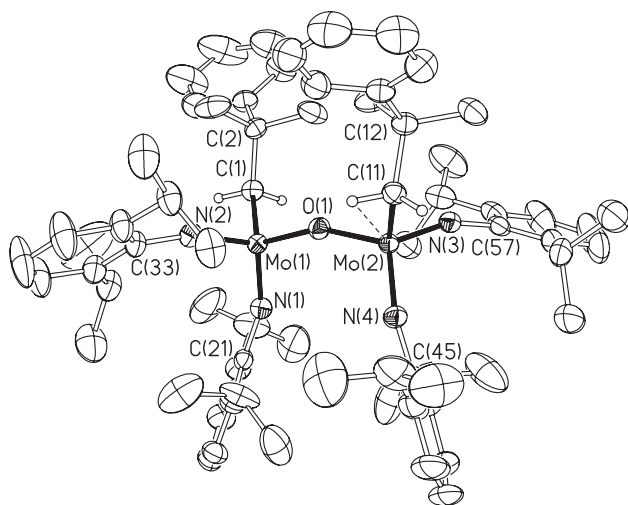


Fig. 4. Molecular structure of **10**, without most H atoms and minor disorder components, and with key atoms labelled.

contain a doublet (<sup>3</sup>J<sub>HP</sub> 4.5 Hz) for the methyl groups at ca. 0.8 ppm (<sup>1</sup>H), and a singlet (ca. –36.5 ppm) in the <sup>31</sup>P NMR spectrum.

Interaction of **1** with LiNHAr in diethyl ether at –78 °C gives an orange solution from which Mo(NHAr)(NAr)<sub>2</sub>(CH<sub>2</sub>CMe<sub>2</sub>Ph)] (**9**) can be isolated together with a second product {[Mo(NAr)<sub>2</sub>(CH<sub>2</sub>CMe<sub>2</sub>Ph)]<sub>2</sub>(μ-O)} (**10**), which has been structurally characterized (Fig. 4, Table 6). The molecule (approximate C<sub>2</sub> axis through O(1)) consists of two tetrahedral [Mo(NAr)<sub>2</sub>(CH<sub>2</sub>CMe<sub>2</sub>Ph)] fragments linked by a pseudo-linear oxo bridge (Mo–O–Mo = 157.61(9)°). The similar Mo–N(imido) bond lengths 1.7467(19)–1.7572(19) Å and Mo–N–C angles 156.23(16)°–164.57(18)° are consistent with all imido ligands acting as four-electron donors. There is evidence of an α-agostic interaction involving Mo(2): Mo(2)–H(11A) 2.51(3) Å, Mo(2)–H(11B) 2.67(3) Å. Disorder in the alkyl group attached to Mo(1) precludes an assessment of any α-agostic interaction for it. The Mo–C–C angles of 117.37(17)° and 118.05(16)° are somewhat smaller than those found in **4** (126.49(12)°) and **5** (125.87(14)°), doubtless a reflection of the lack of steric congestion provided by the presence of the oxo ligand (cf. **1** (115.55(12)°). A number of systems involving μ-O ligation in the presence of terminal imido groups have been structurally characterised [6]. The origin of the oxo group in **10** is uncertain. It is possible that oxygen could be extracted from the solvent diethyl

Table 6  
Selected bond lengths (Å) and angles (°) for **10**.C<sub>5</sub>H<sub>12</sub>

Mo(1)–O	1.9010(15)	Mo(1)–C(1)	2.150(2)
Mo(1)–N(1)	1.7572(19)	Mo(1)–N(2)	1.7467(19)
Mo(2)–O	1.8996(15)	Mo(2)–C(11)	2.143(2)
Mo(2)–N(3)	1.7528(19)	Mo(2)–N(4)	1.7511(19)
N(1)–C(21)	1.397(3)	N(2)–C(33)	1.392(3)
N(3)–C(57)	1.395(3)	N(4)–C(45)	1.401(3)
O–Mo(1)–C(1)	114.17(8)	O–Mo(1)–N(1)	113.77(8)
O–Mo(1)–N(2)	113.93(8)	C(1)–Mo(1)–N(1)	102.11(8)
C(1)–Mo(1)–N(2)	101.92(9)	N(1)–Mo(1)–N(2)	109.72(9)
O–Mo(2)–C(11)	111.31(8)	O–Mo(2)–N(3)	113.43(8)
O–Mo(2)–N(4)	113.19(8)	C(11)–Mo(2)–N(3)	104.30(9)
C(11)–Mo(2)–N(4)	102.91(9)	N(3)–Mo(2)–N(4)	110.84(9)
Mo(1)–O–Mo(2)	157.61(9)	Mo(1)–C(1)–C(2)	117.37(17)
Mo(1)–C(1)–C(2A)	118.4(3)	Mo(2)–C(11)–C(12)	118.05(15)
Mo(1)–N(1)–C(21)	156.23(16)	Mo(1)–N(2)–C(33)	164.57(18)
Mo(2)–N(3)–C(57)	160.24(17)	Mo(2)–N(4)–C(45)	162.46(18)

ether; however, the formation of oxo species from water is well known; Sundermeyer et al. [7] have demonstrated the complete conversion of imido molybdenum species to their oxo counterparts.

In conclusion, the chemistry described herein shows that complexes of the form  $[\text{MoCl}(\text{NAr})_2\text{R}]$  ( $\text{R} = \text{CH}_2\text{CMe}_2\text{Ph}$  or  $\text{CH}_2\text{CMe}_3$ ;  $\text{Ar} = 2,6\text{-Pr}_2\text{C}_6\text{H}_3$ ) provide a useful entry, via chloride substitution reactions, to four- and five-coordinate bis(imido) monoalkyl chemistry.

### 3. Experimental

#### 3.1. General

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Durham, Medac Ltd. and at Imperial College. NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400.0 MHz ( $^1\text{H}$ ), 100.6 MHz ( $^{13}\text{C}$ ) and 100.0 MHz ( $^{31}\text{P}$ ); chemical shifts are referenced to the residual protio impurity of the deuterated solvent. IR spectra (nujol mulls, KBr or CsI windows) were recorded on Perkin–Elmer 577 and 457 grating spectrophotometers.  $[\text{MoCl}_2(\text{NAr})_2(\text{dme})]$  and  $[\text{MoCl}_2(\text{NBu}^t)(\text{NAr})(\text{dme})]$  were prepared by literature methods [8,9]. Trimethylphosphine was prepared by the method of Wolfsberger and Schmidbauer [10]. Grignard reagents were prepared from RCl and activated Mg in diethyl ether. All other chemicals were obtained commercially and used as received unless stated otherwise.

#### 3.2. Preparation of $[\text{MoCl}(\text{NAr})_2\text{CH}_2\text{CMe}_2\text{Ph}]$ (1)

To a solution of  $[\text{MoCl}_2(\text{NAr})_2(\text{dme})]$  (5.04 g, 8.3 mmol) in diethyl ether (ca. 100  $\text{cm}^3$ ) at  $-78^\circ\text{C}$  was slowly added (over about 20 min)  $\text{CH}_2\text{CMe}_2\text{PhMgCl}$  (12.2  $\text{cm}^3$ , 0.68 M solution, 8.3 mmol) in diethyl ether (ca. 10  $\text{cm}^3$ ). After slowly warming to ambient temperature and stirring for 12 h the orange suspension was filtered. The remaining solid was further extracted with diethyl ether ( $2 \times 50 \text{ cm}^3$ ) and pentane (50  $\text{cm}^3$ ). The volatiles were removed from the combined extracts, affording a red solid. Extraction into pentane (ca. 60  $\text{cm}^3$ ) and cooling ( $-78^\circ\text{C}$ ) gave **1** as orange–red crystals. Yield: 3.28 g, 64%. Found: C, 66.17; H, 7.80; N, 4.71%.  $\text{MoClN}_2\text{C}_{34}\text{H}_{47}$  requires C, 66.39; H, 7.70; N, 4.55%. IR: 1599w, 1576m, 1569m, 1494m, 1467s, 1461s, 1456s, 1451s, 1446s, 1425s, 1377s, 1360s, 1324s, 1289s, 1273s, 1223m, 1190m, 1175m, 1158m, 1144m, 1103s, 1057s,

1043s, 1029s, 982s, 933m, 903w, 840w, 798s, 768m, 753s, 723m, 701s, 649w, 631w, 619w, 593w, 568m, 550s, 537s.

#### 3.3. Preparation of $[\text{MoCl}(\text{NAr})_2(\text{CH}_2\text{CMe}_3)]$ (2)

As for **1**, but using  $[\text{MoCl}_2(\text{NAr})_2(\text{dme})]$  (5.04 g, 8.3 mmol) and  $\text{Me}_3\text{CCH}_2\text{MgCl}$  (10.4  $\text{cm}^3$ , 0.8 M, 8.3 mmol). Yield: 40%. Found: C, 61.37; H, 7.75; N, 5.47%.  $\text{MoClN}_2\text{C}_{29}\text{H}_{45}$  requires C, 62.98; H, 8.20; N, 5.06%. IR: 3058m, 2724m, 2660m, 1921w, 1858w, 1619w, 1585w, 1572w, 1520w, 1364 s, 1261m, 1231w, 1177w, 1143w, 1098m, 1056m, 1045m, 1018m, 934w, 863w, 797 vs, 754s, 662vw, 634vw, 618vw, 580vw, 561vw, 535w, 505vw, 488vw, 461w, 386 vw, 374w, 352s, 328m. M.S. (CI): 590  $[\text{M} + \text{H} + \text{Cl}]^+$ , 554  $[\text{M} + \text{H}]^+$ , 482  $[\text{M} - \text{CH}_2\text{CMe}_3]^+$ , 440  $[\text{M} - \text{CH}_2\text{CMe}_3 - i\text{Pr}]^+$ ; (EI,  $m/z$ ): 589  $[\text{M} + \text{Cl}]^+$ , 554  $[\text{M} + \text{H}]^+$ , 482  $[\text{M} - \text{CH}_2\text{CMe}_3]^+$ , 440  $[\text{M} - \text{CH}_2\text{CMe}_3 - i\text{Pr}]^+$ .

#### 3.4. Preparation of $[\text{MoCl}(\text{NAr})(\text{NBu}^t)(\text{CH}_2\text{CMe}_2\text{Ph})]$ (3)

As for **1**, but using  $[\text{MoCl}_2(\text{NAr})(\text{NBu}^t)(\text{dme})]$  (4.88 g, 9.7 mmol) and  $\text{PhMe}_2\text{CCH}_2\text{MgCl}$  (12.9  $\text{cm}^3$ , 0.75 M, 9.7 mmol). Yield: 3.5 g, 71%. Found: C, 60.96; H, 7.74; N, 5.43%.  $\text{MoN}_2\text{C}_{26}\text{H}_{39}$  requires C, 61.11; H, 7.69; N, 5.48%. IR: 3057m, 2725m, 2670m, 1599m, 1581w, 1494m, 1452vs, 1361vs, 1331s, 1308 m, 1283 s, 1215vs, 1190m, 1158w, 1132m, 1116w, 1030m, 982s, 934m, 903w, 805w, 794w, 753s, 697s, 668w, 615w, 592w, 552w, 514w, 454w, 443w, 384m, 357w, 338s, 324m. M.S. (CI) 512  $[\text{M} + \text{H}]^+$ ; (EI) 511  $[\text{M}]^+$ , 476  $[\text{M} - \text{Cl} + \text{H}]^+$ , 378  $[\text{M} - \text{CH}_2\text{CMe}_2\text{Ph}]^+$ .

#### 3.5. Preparation of $[\text{MoCp}(\text{NAr})_2(\text{CH}_2\text{CMe}_2\text{Ph})]$ (4)

To **1** (1.02 g, 1.66 mmol) and LiCp (0.12 g, 1.66 mmol) was added cold ( $-78^\circ\text{C}$ ) diethyl ether (ca. 30  $\text{cm}^3$ ). After stirring for 24 h, the volatiles were removed and the dark red solid was extracted into pentane; cooling ( $-40^\circ\text{C}$ ) afforded **4**. Yield: 0.52 g, 49%. Found: C, 72.72; H, 8.35; N, 4.47%.  $\text{MoN}_2\text{C}_{39}\text{H}_{52}$  requires C, 72.65; H, 8.13; N, 4.56%. IR: 3129w, 3088w, 3052w, 1599w, 1586m, 1494m, 1422s, 1360s, 1336, 1262s, 1224m, 1192m, 1175m, 1159m, 1136m, 1098s, 1075m, 1062m, 1033m, 1020m, 966s, 931m, 834w, 806s, 768s, 746s, 704s, 615w, 599w, 561m, 538m. M.S. (CI) 647  $[\text{M} + \text{H}]^+$ , 513  $[\text{M} - \text{CH}_2\text{CMe}_2\text{Ph}]^+$ , 471  $[\text{M} - \text{CH}_2\text{CMe}_2\text{Ph} - \text{CHCMe}_2]^+$ , 350  $[\text{M} - \text{CH}_2\text{CMe}_2\text{Ph} - \text{C}_5\text{H}_5]^+$ ; (EI,  $m/z$ ) 646  $[\text{M}]^+$ , 513  $[\text{M} - \text{CH}_2\text{CMe}_2\text{Ph}]^+$ ; (FAB $^+$ ,  $m/z$ ) 646  $[\text{M}]^+$ , 513  $[\text{M} - \text{CH}_2\text{CMe}_2\text{Ph}]^+$ .

#### 3.6. Preparation of $[\text{MoInd}(\text{NAr})_2(\text{CH}_2\text{CMe}_2\text{Ph})]$ (5)

As for **4**, but using **1** (0.77 g, 1.25 mmol) and Li(Indenyl) (0.15 g, 1.25 mmol), affording **5** as red prisms.

Yield: 0.56 g, 64%. Found: C, 66.42; H, 6.63; N, 4.59%.  $\text{MoN}_2\text{C}_{34}\text{H}_{51}$  requires C, 66.38; H, 6.92; N, 4.69%. IR: 2556w, 2721w, 2692w, 2612w, 2360w, 2342w, 1949w, 1939w, 1912w, 1707w, 1694w, 1666w, 1651w, 1634w, 1622w, 1597m, 1596m, 1567m, 1539w, 1513w, 1493s, 1463s, 1456s, 1435s, 1429s, 1418s, 1377s, 1359s, 1322s, 1304s, 1284s, 1261s, 1224s, 1186s, 1178s, 1158m, 1151m, 1101s, 1087m, 1059s, 1045m, 1034s, 1001w, 975s, 942s, 909m, 841m, 805s, 798m, 765s, 757s. M.S. (CI) 696  $[\text{M} + \text{H}]^+$ ; (EI,  $m/z$ ) 695  $[\text{M}]^+$ , 580  $[\text{M} - \text{C}_9\text{H}_7]^+$ , 443  $[\text{M} - \text{C}_9\text{H}_7 - \text{C}_6\text{H}_3\text{Pr}_2]^+$ ; (FAB<sup>+</sup>,  $m/z$ ) 695  $[\text{M}]^+$ , 580  $[\text{M} - \text{C}_9\text{H}_7]^+$ , 443  $[\text{M} - \text{C}_9\text{H}_7 - \text{C}_6\text{H}_3\text{Pr}_2]^+$ .

### 3.7. Preparation of $[\text{Mo}(\text{O}i\text{Bu}^t)(\text{N}Ar)_2(\text{CH}_2\text{CMe}_2\text{Ph})]$ (**6**)

To **1** (0.98 g, 1.6 mmol) and  $\text{LiO}i\text{Bu}^t$  (0.13 g, 1.6 mmol) was added cold ( $-78^\circ\text{C}$ ) diethyl ether. After stirring at  $25^\circ\text{C}$  for 12 h, the volatiles were removed in vacuo, and the residue was extracted with pentane (ca.  $20\text{ cm}^3$ ). Cooling ( $-40^\circ\text{C}$ ) afforded **6** as red needles. Yield 0.43 g, 42%. Found: C, 69.96; H, 8.37; N, 4.60%.  $\text{MoON}_2\text{C}_{38}\text{H}_{56}$  requires C, 69.92; H, 8.65; N, 4.29%. IR: 3056m, 2754w, 2722w, 2671w, 1599m, 1584m, 1569m, 1539w, 1516w, 1495m, 424s, 1361s, 1324s, 1278vs, 1250s, 1235m, 1224m, 1168s, 1100m, 1072m, 1057m, 1045m, 1032m, 982vs, 952vs, 838w, 787s, 751vs, 711m, 698s, 661w, 635w, 596m, 571m, 563m, 538w, 505m, 476vw, 449w, 428w. M.S. (CI) 654  $[\text{M} + \text{H}]^+$ , 596  $[\text{M} - i\text{Bu}]^+$ ; (EI,  $m/z$ ) 786  $[\text{M} + \text{CH}_2\text{CMe}_2\text{Ph}]^+$ , 726  $[\text{M} + \text{O}^t\text{Bu}]^+$ , 654  $[\text{M} + \text{H}]^+$ , 596  $[\text{M} - i\text{Bu}]^+$ , 580  $[\text{M} - \text{O}^t\text{Bu}]^+$ , 520  $[\text{M} - \text{CH}_2\text{CMe}_2\text{Ph}]^+$ , 463  $[\text{M} - \text{CH}_2\text{CMe}_2\text{Ph} - i\text{Bu}]^+$ .

### 3.8. Preparation of $[\text{MoMe}(\text{N}Ar)_2(\text{CH}_2\text{CMe}_2\text{Ph})]$ (**7**)

As for **6**, but using **1** (1.02 g, 1.66 mmol) and  $\text{MeMgI}$  ( $0.55\text{ cm}^3$ , 3.0 M solution, 1.66 mmol), affording **7** as orange crystals. Yield: 0.45 g, 46%. Sticky nature of product resulted in inconsistent microanalysis. IR: 3054s, 2721m, 1599m, 1576m, 1569m, 1494m, 1467vs, 1456vs, 1451vs, 1446vs, 1425s, 1360s, 1324s, 1289m, 1273s, 1223m, 1190m, 1175m, 1158m, 1144m, 1103s, 1057m, 1043m, 1029m, 982m, 933m, 903w, 865w, 856w, 840w, 798s, 768m, 753vs, 701s, 666w, 649w, 631w, 619m, 593m. M.S. (CI) 596  $[\text{M} + \text{H}]^+$ , 581  $[\text{M} - \text{CH}_3 + \text{H}]^+$ , 477  $[\text{M} - \text{CMe}_2\text{Ph} + \text{H}]^+$ , 463  $[\text{M} - \text{CH}_2\text{CMe}_2\text{Ph} + \text{H}]^+$ .

### 3.9. Preparation of $[\text{MoMe}(\text{PMe}_3)(\text{N}Ar)_2(\text{CH}_2\text{CMe}_2\text{Ph})]$ (**8**)

Pentane ( $30\text{ cm}^3$ ) was added to an ampoule charged with **7** (0.5 g, 0.84 mmol). The resultant red solution was frozen ( $-198^\circ\text{C}$ ) and placed under vacuum. Trimethylphosphine (0.076 g, 1.0 mmol) was added to the solution (vacuum-transfer) and the mixture was allowed to warm slowly to room temperature. The dark orange

solution obtained was filtered and concentrated under reduced pressure. Cooling ( $-35^\circ\text{C}$ ) overnight afforded **8** as an orange microcrystalline solid (Yield: 0.30 g, 53%). Found: C, 67.85; H, 8.96; N, 4.19%.  $\text{MoPN}_2\text{C}_{38}\text{H}_{59}$  requires C, 68.04; H, 8.87; N, 4.18%. IR: 3028m, 2721w, 1597m, 1586m, 1567m, 1539w, 1493s, 1456vs, 1435vs, 1429vs, 1418vs, 1359vs, 1322vs, 1304s, 1284vs, 1261vs, 1224m, 1186m, 1178m, 1158m, 1151m, 1101s, 1087m, 1059s, 1045m, 1034s, 1001vw, 975vs, 942vs, 909m, 841m, 805m, 798m, 765vs, 757vs, 700vs, 667m, 615m.  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ , 298K):  $\delta$   $-36.49$  (s,  $\text{PMe}_3$ ).

### 3.10. Preparation of $[\text{Mo}(\text{N}HAr)(\text{N}Ar)_2(\text{CH}_2\text{CMe}_2\text{Ph})]$ (**9**)

Chilled ( $-78^\circ\text{C}$ ) diethyl ether was added to a solid mixture of **1** (0.59 g, 9.6 mmol) and  $\text{LiNH}Ar$  (0.18 g, 9.6 mmol) at  $-78^\circ\text{C}$ . The resultant solution was allowed to warm to room temperature, stirred for 1 h and then filtered. Volatiles were removed in vacuo and extraction into pentane followed by cooling ( $-35^\circ\text{C}$ ) afforded orange crystals of **9**. Yield: 0.32 g, 44%. Found: C, 72.43; H, 8.46; N, 5.35%.  $\text{MoN}_3\text{C}_{46}\text{H}_{65}$  requires C, 73.08; H, 8.67; N, 5.56%. IR: 3303m, 1569m, 1362m, 1320s, 1287m, 1267s, 1245m, 1223m, 1191s, 1158m, 1109m, 1071m, 1056m, 1044m, 1031m, 981s, 932m, 904m, 886m, 855s, 837w, 796s, 764m, 750vs, 697s, 634w, 625w, 552m, 508m, 480m, 456w, 421m. M.S. (CI) 756  $[\text{M}]^+$ ; (EI,  $m/z$ ) 756  $[\text{M}]^+$ , 624  $[\text{M} - \text{CH}_2\text{CMe}_2\text{Ph}]^+$ , 581  $[\text{M} - \text{CH}_2\text{CMe}_2\text{Ph} - \text{CHCMe}_2]^+$ .

### 3.11. Preparation of $\{[\text{Mo}(\text{N}Ar)_2(\text{CH}_2\text{CMe}_2\text{Ph})]_2(\mu\text{-O})\}$ (**10**)

#### 3.11.1. From $\text{LiNH}Ar$

To an ampoule charged with a solid mixture of **1** (0.59 g, 0.96 mmol) and  $\text{LiNH}Ar$  (0.18 g, 0.96 mmol) at  $-78^\circ\text{C}$  was added chilled ( $-78^\circ\text{C}$ ) diethyl ether ( $50\text{ cm}^3$ ). The resultant solution was allowed to warm to room temperature and stirred for 48 h. All volatile components were removed under reduced pressure and the mixture heated to  $50^\circ\text{C}$  for 12 h. The reaction mixture was then redissolved in diethyl ether ( $50\text{ cm}^3$ ), stirred for a further 48 h, volatile components removed under reduced pressure, then heated to  $50^\circ\text{C}$ . This process was repeated a further three times. The resultant dark red oil was extracted into minimal pentane and cooled to  $-35^\circ\text{C}$ , affording red-orange, solvent-dependent crystals of **10** (Yield: 0.73 g, 65%).

#### 3.11.2. From $\text{LiNH}i\text{Bu}^t$

Chilled ( $-78^\circ\text{C}$ ) diethyl ether was added to a solid mixture of **1** (0.95 g, 1.54 mmol) and  $\text{LiNH}i\text{Bu}^t$  (0.122 g, 1.54 mmol) at  $-78^\circ\text{C}$ . The resultant solution was al-

Table 7  
Crystallographic data

Compound	<b>1</b>	<b>4</b>	<b>5</b>	<b>10</b> · pentane
Formula	C <sub>34</sub> H <sub>47</sub> ClMoN <sub>2</sub>	C <sub>39</sub> H <sub>52</sub> MoN <sub>2</sub>	C <sub>43</sub> H <sub>54</sub> MoN <sub>2</sub>	C <sub>68</sub> H <sub>94</sub> Mo <sub>2</sub> N <sub>4</sub> O · C <sub>5</sub> H <sub>12</sub>
<i>M</i>	615.1	644.8	694.8	1247.5
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	16.6488(13)	17.5013(12)	12.8531(9)	12.5275(5)
<i>b</i> (Å)	16.2054(13)	11.3724(8)	26.3545(17)	13.3471(6)
<i>c</i> (Å)	11.9638(9)	19.2673(14)	11.1511(8)	21.2886(9)
$\alpha$ (°)				78.547(2)
$\beta$ (°)	92.260(2)	113.065(1)	83.159(2)	
$\gamma$ (°)				86.315(2)
<i>U</i> (Å <sup>3</sup> )	3225.3(4)	3528.3(4)	3777.3(5)	3460.8(3)
<i>Z</i>	4	4	4	2
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.267	1.214	1.222	1.197
$\mu$ (mm <sup>-1</sup> )	0.51	0.40	0.38	0.41
Data measured	19 428	23 377	24 256	27 405
Unique data	7350	8096	8790	15 259
<i>R</i> <sub>int</sub>	0.0319	0.0266	0.0203	0.0168
Parameters	374	422	432	854
<i>R</i> ( <i>F</i> , <i>F</i> <sup>2</sup> > 2 $\sigma$ )	0.0270	0.0297	0.0262	0.0350
<i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> , all data)	0.0712	0.0710	0.0650	0.0893
Max., min. el. density (eÅ <sup>-3</sup> )	0.38, -0.51	0.39, -0.55	0.48, -0.40	0.88, -0.56

lowed to warm to room temperature and stirred for 2 days. All volatiles were removed in vacuo and the resultant solid redissolved in diethyl ether (50 cm<sup>3</sup>) and stirred for a further 2 days. This process was repeated a further three times. The resultant orange solid was extracted into pentane and cooled (-35 °C) to afford orange, solvent-dependent crystals of **10** (Yield: 1.11 g, 61%). Found: C, 69.43; H, 8.26; N, 4.95%. Mo<sub>2</sub>ON<sub>4</sub>C<sub>68</sub>H<sub>94</sub> requires C, 69.49; H, 8.06; N, 4.77%. IR: 3054m, 1598w, 1568m, 1495m, 1424vs, 1362m, 1333s, 1322s, 1273s, 1223w, 1178w, 1158w, 1100m, 1076m, 1058m, 1045m, 1031m, 983m, 933w, 903w, 796s, 770vs, 698m, 644w, 594w, 559w, 537w, 456w. M.S. (EI) 604 [1/2M + O]<sup>+</sup>.

### 3.12. Preparation of Mo(*NAr*)<sub>2</sub>(CH<sub>2</sub>CMe<sub>2</sub>Ph)(*NH*Bu<sup>t</sup>) (**11**)

Chilled (-78 °C) diethyl ether was added to a solid mixture of **1** (0.95 g, 1.55 mmol) and LiNHBu<sup>t</sup> (0.12 g, 1.55 mmol) at -78 °C. The resultant solution was allowed to warm to room temperature and stirred for 1 h. The resultant dark orange solution was filtered from the white precipitate and all volatile components removed under reduced pressure, yielding an orange solid. Extraction into pentane followed by removal of volatiles in vacuo afforded **11** as an orange oil (yield: 0.41 g, 41%). IR: 3265m, 3057s, 3021s, 2965–2869vs, 2802w, 1599m, 1586w, 1570vw, 1495s, 1446vs, 1425vs, 1382s, 1361s, 1337vs, 1324vs, 1275vs, 1262vs, 1206s, 1158m, 1143m, 1100, 1057s, 1045s, 1030vs, 1020vs, 983s, 970s, 933m, 909m, 867w, 840w, 797s, 785s, 768s, 751s, 736m 700s,

657m, 623m, 602m, 586m, 554m, 539w, 452w, 436w. M.S. (EI): 595 [M-C(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>.

### 3.13. X-ray crystallography

Table 7 gives information on the crystal structure determinations for **1**, **4**, **5** and **10**. All data were measured at 160 K with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Siemens SMART CCD diffractometer, using fine-slice  $\omega$  scans [11]. Corrections for absorption were based on multiple and symmetry-equivalent reflections [12]. The structures were solved by direct methods, and refined on *F*<sup>2</sup> values for all unique data. Anisotropic displacement parameters were refined for all non-hydrogen atoms except low-occupancy disorder components, and H atoms were constrained except for metal-bonded CH<sub>2</sub> groups, which were freely refined to investigate  $\alpha$ -agostic interactions. Two-fold disorder was resolved and refined for some isopropyl substituents, and for one complete ligand in **10**, with the aid of restraints. For the non-centrosymmetric **5**, the absolute structure was confirmed by refinement of an enantiopole parameter to 0.00(2) [13].

## 4. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 217025, 217026, 217027 and 217028 for compounds **1**, **4**, **5** and **10**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CD2 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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