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Organotransition-metal complexes of multidentate ligands

XVI *. On the nature of the sigma-donicity of the saturated nitrogen ligands; chelate-assisted weakening of the α-N–H bond: synthesis, and spectral and structural study of $[Mo(N-N)(CO)_4]$ (N–N = saturated nitrogen bidentate ligands)

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Abstract

A series of complexes, $[Mo(N-N)(CO)_4]$ (N–N = saturated nitrogen bidentate ligands), were prepared from $[Mo(pip)_2(CO)_4]$ (pip = piperidine) and N–N in CH_2Cl_2 at 40 °C. The structure of $[Mo((PhCH_2)HNCH_2CH_2NMe_2)(CO)_4]$ was also determined by X-ray crystallography: space group *Pbca*, $a = 14.895(7)$, $b = 11.947(4)$, $c = 19.189(8)$ Å, $V = 3415(2)$ Å^3, $Z = 8$, $d_{calc} = 1.503$ g/cm^3, $R = 0.026$ and $R_w = 0.026$ based on 1646 reflections with $I > 3.0\ \sigma(I)$. Both the spectral and structural data of the complexes indicate that the electron-density donating from the ligands comprises not only the lone electron pair of the nitrogen atom but the electron-density deprived from the neighboring groups by the highly electronegative nitrogen atom. These data also show that the more electron density of the α-N–H bond relative to that of the α-N–R bond (R = alkyl or aryl) is removed upon coordination of the nitrogen donor ligands, apparently explaining why a chelate-assisted oxidative addition of the N–H bond occurs more readily than the N–R bond through prior coordination and concurrent weakening of the N–H bond.

Introduction

Analysis of ligand effects, especially the electronic parameters of ligands, has been one of the important research topics in delineating kinetics and thermodynamics of organometallic reactions for many years [2–4]. However, only a few

* For Part XV, see ref. 1.

Table 1

Analytical and IR data for $[Mo(N-N)(CO)_4]$

N–N	Anal. Found (calc.) (%)			IR [a] observed (averaged) (cm^{-1})		
	C	H	N	[ν(NH)] [b]	[ν(CO)] [b]	[ν(CO)] [c]
$(PhCH_2)HNCH_2CH_2NMe_2$	46.24 (36.64)	4.70 (4.70)	7.24 (7.25)	3280	2016, 1887, 1854, 1790 (1887)	2016, 1886, 1869(sh), 1826
$MeHNCH_2CH_2NMe_2$	34.80 (34.85)	4.71 (4.55)	8.93 (9.03)	3304	2012, 1888, 1856, 1806 (1891)	2016, 1886, 1874(sh), 1826
$Me_2NCH_2CH_2NH_2$	32.42 (32.45)	4.08 (4.08)	9.40 (9.46)	3372, 3316 (3344)	2020, 1900, 1880, 1790 (1898)	2016, 1888, 1873(sh), 1824
$MeHNCH_2CH_2NHMe$	32.42 (32.45)	4.06 (4.08)	9.36 (9.46)	3304	2016, 1904, 1856, 1784 (1890)	2016, 1888, 1870(sh), 1826
$Me_2NCH_2CH_2CH_2NH_2$	34.33 (34.85)	4.60 (4.55)	9.01 (9.03)	3356, 3300 (3328)	2016, 1892, 1872, 1798 (1895)	2016, 1888, 1868(sh), 1820

[a] ν(NH) band in medium intensity; the ν(CO) band higher than 2000 cm^{-1} in medium intensity; other ν(CO) bands in strong or very strong intensity or in a shoulder, specified by abbreviation (sh), see text. [b] In KBr discs. [c] In CH_2Cl_2.

reports in the literature are concerned with the real nature of the electron donating or accepting of phosphorus ligands by collecting either orbital or structural evidence [3,4]. In this report, we supply IR and structural evidence showing that the electron donating nature of saturated nitrogen ligands in some metal carbonyl derivatives is related to the substituents on the nitrogen atom. This study also leads us to find that the coordination of nitrogen ligands can weaken the α-N–H bond more than the α-N–R bond (R = alkyl or aryl), accounting for why a chelate-assisted oxidative addition of the α-N–H bond occurs more readily than the α-N–R bond [5]. We believe that the accumulated understanding on activation of N–H bonds may help to develop systems for catalytic functionalization of ammonia and other ammines [6].

Results and discussion

It is well established that reflux of a mixture of $[Mo(CO)_6]$ and the bidentate ligand containing an acidic hydrogen atom at high temperatures can result in oxidative decarbonylation, giving multiple metal–metal bonded compounds when only one non-hydrogen atom is bonded between the two ligating atoms of the ligand [7]. Accordingly, we employed a method suggested earlier by Darensbourg and Kump [8] to prepare $[Mo(N–N)(CO)_4]$. This orange-yellow product can often be obtained in ca. 60% yield from the mixture of $[Mo(pip)_2(CO)_4]$ (pip = piperidine) and N–N in equal quantity heated at 40 °C for 20 min in CH_2Cl_2. The low yield is probably due to the high air-sensitivity of this complex, because a freshly prepared $[Mo(pip)_2(CO)_4]$ can give $[Mo(N–N(CO)_4]$ in higher yield.

The compounds are well characterized as *cis*-$[Mo(N–N)(CO)_4]$ by a combination of elemental analysis, IR and NMR spectral results. The solution IR spectra of the compounds (Table 1) are similar to each other in containing four carbonyl stretching bands. The bands of medium, very strong, strong as a shoulder, and strong intensity by decreasing frequencies are what we expect for *cis*-$[ML_2(CO)_4]$ [9], where M represents a transition-metal atom and L_2 can be one bidentate or two monodentate ligands. The more downfield chemical shifts observed in the NMR spectra for the protons of the free relative to the bound N–N ligand indicate that both nitrogen atoms have bonding interactions with the central metal atom in the compounds. This feature is further supported by the X-ray crystal structure of $[Mo\{(PhCH_2)HNCH_2CH_2NMe_2\}(CO)_4]$ (Fig. 1).

A careful comparison between the solution and solid-state IR data (Table 1) reveals that the carbonyl stretching frequencies of the compounds in solution are very similar to each other while the stretching values obtained in the solid state are different from each other. Apparently, extensive solvent effects probably involving the local dipole–dipole interactions between the compounds and solvent molecules [10] broaden the vibration bands so that no characteristic bands were observed for the compounds measured in solution. (Unfortunately, the compounds are not soluble in hydrocarbon solvents such as hexane and no spectral data in the solvents can be compared with those in the solid state.) We thus chose to use the solid-state data in our discussion about sigma-donicity of N–N, although the solution data were used previously by Strohmeier [11] or Tolman [12] to describe the electron-acceptor or -donor ability of the phosphorus ligands. Since the ligand, N–N, may have two N–H bonds in either one or two different nitrogen atoms (Table 1), one

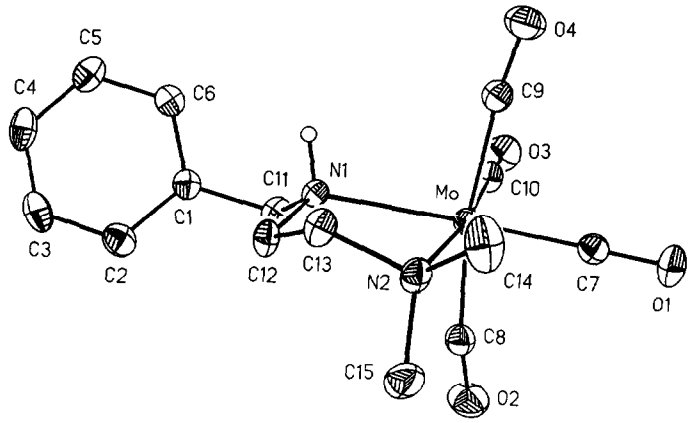

Fig. 1. ORTEP plot of $[Mo\{(PhCH_2)HNCH_2CH_2NMe_2\}(CO)_4]$ showing the atomic numbering scheme and 50% probability thermal ellipsoids. The unlabelled sphere is the hydrogen atom.

or two (or more) carbonyl stretching frequencies for $[Mo(N\text{–}N)(CO)_4]$ may be under the different influence of the electron donation of N–N through the metal to CO backbonding, depending on the relative positions of the carbonyl groups with respect to N–N in the compounds [13]. Hence, we decided to use the average carbonyl stretching frequency, $[\bar{\nu}(CO)]$, and the average N–H stretching value, $[\bar{\nu}(NH)]$, in the comparison, rather than choose one frequency as used previously by Tolman in his mono-substituted metal carbonyl complexes [12].

As observed in Fig. 2, a rather good correlation between $[\bar{\nu}(NH)]$ and $[\bar{\nu}(CO)]$ for the complexes measured in the solid state is obtained, supporting the validity of our decision in using the averaged solid-state data. More importantly, the correlation indicates that the major part, if not all, of the electron density, which is deprived from the N–H bond, is used to backdonate from the central metal atom to the carbonyl groups in the compounds. This argument can find supporting evidence from the structural details of $[Mo\{(PhCH_2)HNCH_2CH_2NMe_2\}(CO)_4]$ (Fig. 1). (The more electron-releasing hydrogen atom relative to the R group was noted in 1971 [14] while little net electron transfer from the methyl group to other systems such as ethylene or benzene was also reported in 1974 by employing various molecular orbital calculations [15].) Indeed, the crystal structure with relevant atomic coordinates (Table 3) reveals that the Mo–N(1) bond length of 2.317(3) Å (Table 4) is significantly shorter as expected than that of 2.342(3) Å for Mo–N(2), although steric factor may also contribute to lengthen the Mo–N bond length for NR_2 than for N(H)R. The bond lengths of 1.932(5) Å for Mo–C(7) and 1.172(5) Å for C(7)–O(1), *trans* to N(1), versus those of 1.953(4) Å for Mo–C(10), and 1.156(5) Å for C(10)–O(3), *trans* to N(2), reflect different metal-to-CO backbonding.

Since the closest intermolecular contacts in the crystal of the compound involving the only nitrogen-bonded hydrogen atom, H(1A), shown as an unlabelled sphere in Fig. 2, are H(1A) ··· O(1), 5.74 Å; H(1A) ··· O(2), 5.02 Å; H(1A) ··· O(3), 4.20 Å and H(1A) ··· O(4), 3.69 Å, an intermolecular hydrogen bond between the nitrogen-bonded hydrogen atom of one molecule and a carbonyl

Table 2

^{1}H NMR data for the bidentate ligand (N–N) and the corresponding complex {[Mo(N–N)(CO)$_4$]}

Compound	^{1}H NMR (ppm) [a]		
	–NH	–$(CH_2)_n$– [b]	–NR_2 [c]
$(PhCH_2)HNCH_2CH_2NMe_2$	1.90 (1H, s)	2.40 (2H, m), 2.67 (2H, m)	2.17 (6H, s), 3.78 (2H, s), 7.28 (5H, m)
Complex	3.30 (1H, br)	2.51 (2H, m), 2.65 (2H, m)	2.74 (6H, br), 3.66 (1H, dd, J = 14.1, 11.4) 4.36 (1H, dd, J = 14.1, 3.3), 7.35 (5H, m)
$MeHNCH_2CH_2NMe_2$	1.41 (1H, s)	2.36 (2H, m), 2.65 (2H, m)	2.22 (6H, s), 2.44 (3H, s)
Complex	3.19 (1H, br)	2.53 (2H, m), 3.05 (2H, m)	2.71 (3H, d, J = 3.6), 2.73 (6H, br)
$Me_2NCH_2CH_2NH_2$	1.27 (2H, s)	2.33 (2H, t, J = 6.1) 2.77 (2H, t, J = 6.1)	2.26 (6H, s)
Complex	2.69 (2H, br)	2.46 (2H, m), 3.01 (2H, m)	2.75 (6H, br)
$MeHNCH_2CH_2NHMe$	1.19 (2H, s)	2.68 (4H, s)	2.43 (6H, s)
Complex	3.01 (2H, br)	2.28 (2H, m), 3.07 (2H, m)	2.71 (6H, d, J = 6.0)
$Me_2NCH_2CH_2CH_2NH_2$	1.21 (2H, s)	1.58 (2H, m) 2.37 (2H, t, J = 6.9) 2.72 (2H, t, J = 6.9)	2.20 (6H, s)
Complex	2.46 (2H, br)	1.78 (2H, m), 2.70 (2H, m) 2.99 (2H, m)	2.68 (6H, br)

[a] Chemical shifts relative to tetramethylsilane. CD_3Cl was used as the NMR solvent. Abbreviations: s, singlet; dd, doublet of doublet; m, multiplet; br, unresolved multiplet or two overlapped singlets; t, triplet. J in hertz. [b] n = 2 or 3. [c] R = $PhCH_2$ or Me.

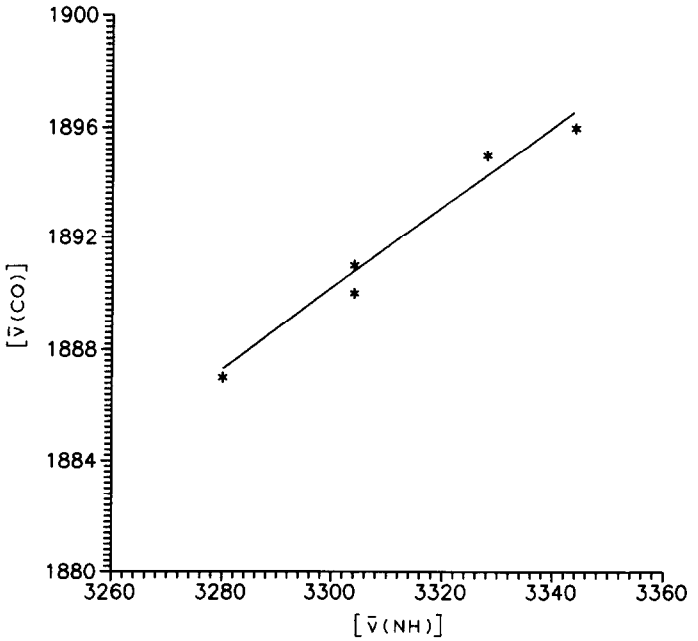

Fig. 2. Variation of $[\bar{\nu}(CO)]$ versus $[\bar{\nu}(NH)]$.

Table 3

Atomic coordinates ($\times 10^4$) and anisotropic displacement coefficients [a] (Å$\times 10^3$) for [Mo{$(PhCH_2)$-$HNCH_2CH_2NMe_2$}$(CO)_4$]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	141(1)	1019(1)	6825(1)	38(1)	38(1)	44(1)	0(1)	−2(1)	0(1)
O(1)	1150(2)	−882(3)	7600(2)	63(2)	57(2)	78(2)	4(2)	−6(2)	24(2)
O(2)	768(2)	−391(3)	5519(2)	81(3)	118(4)	81(3)	21(2)	1(2)	−40(3)
O(3)	1972(2)	2237(3)	6654(2)	52(2)	70(3)	97(3)	−14(2)	0(2)	2(2)
O(4)	64(3)	2144(3)	8313(2)	128(3)	69(3)	57(2)	−7(2)	−7(2)	−10(2)
N(1)	−727(2)	2362(3)	6273(2)	40(2)	38(2)	43(2)	1(2)	3(1)	1(2)
N(2)	−1315(2)	295(3)	6921(2)	46(2)	43(2)	62(3)	−4(2)	−4(2)	7(2)
C(1)	−891(3)	3826(4)	5342(2)	47(2)	53(3)	41(2)	0(2)	6(2)	7(2)
C(2)	−1460(3)	3703(5)	4780(2)	71(3)	69(4)	48(3)	−8(3)	0(2)	6(3)
C(3)	−1940(3)	4601(6)	4525(3)	66(3)	101(5)	54(3)	0(3)	−12(3)	22(3)
C(4)	−1864(3)	5636(5)	4827(3)	60(3)	81(5)	71(4)	16(3)	10(3)	41(3)
C(5)	−1305(3)	5770(4)	5386(3)	66(3)	54(4)	70(3)	7(3)	19(3)	13(3)
C(6)	−823(3)	4877(4)	5646(2)	52(3)	58(4)	46(3)	−5(3)	4(2)	6(3)
C(7)	765(3)	−166(4)	7309(2)	45(3)	48(3)	50(3)	−7(2)	0(2)	−1(2)
C(8)	466(3)	140(4)	5957(2)	50(3)	61(4)	59(3)	4(3)	−5(2)	−4(3)
C(9)	38(3)	1775(4)	7765(2)	68(3)	42(3)	54(3)	0(3)	−4(3)	3(2)
C(10)	1288(3)	1788(4)	6714(2)	49(3)	47(3)	53(3)	4(2)	−3(2)	7(2)
C(11)	−349(3)	2866(4)	5627(2)	48(3)	56(4)	58(3)	3(2)	11(2)	3(2)
C(12)	−1640(2)	1905(4)	6161(2)	37(2)	49(3)	67(3)	4(2)	−5(2)	13(2)
C(13)	−1921(3)	1264(4)	6795(2)	43(2)	54(3)	66(3)	2(2)	9(2)	8(3)
C(14)	−1496(3)	−155(5)	7624(3)	63(3)	98(5)	92(4)	−22(3)	0(3)	48(4)
C(15)	−1519(3)	−589(4)	6409(3)	64(4)	55(4)	117(5)	−5(3)	−19(3)	−14(3)

[a] The anisotropic displacement exponent takes the form: $-2\pi^2(h^2a^2 \times U_{11} + \ldots + 2hka \times b \times U_{12})$.

Table 4

Selected bond lengths (Å) and bond angles (°) for [Mo{($PhCH_2$)$HNCH_2CH_2NMe_2$}$(CO)_4$]

Mo–N(1)	2.317(3)	Mo–N(2)	2.342(3)
Mo–C(7)	1.932(5)	Mo–C(8)	2.028(5)
Mo–C(9)	2.022(5)	Mo–C(10)	1.953(4)
O(1)–C(7)	1.172(5)	O92)–C(8)	1.145(6)
O(3)–C(10)	1.156(5)	O(4)–C(9)	1.141(6)
N(1)–C(11)	1.489(5)	N(1)–C(12)	1.482(5)
N(2)–C(13)	1.488(5)	N(2)–C(14)	1.477(6)
N(2)–C(15)	1.475(6)	C(1)–C(2)	1.379(6)
C(1)–C(6)	1.387(7)	C(1)–C(11)	1.506(6)
C(2)–C(3)	1.379(8)	C(3)–C(4)	1.369(9)
C(4)–C(5)	1.367(7)	C(5)–C(6)	1.380(7)
C(12)–C(13)	1.496(6)		
N(1)–Mo–N(2)	77.0(1)	N(1)–Mo–C(7)	174.9(1)
N(2)–Mo–C(7)	97.9(2)	N(1)–Mo–C(8)	96.7(2)
N(2)–Mo–C(8)	95.4(2)	C(7)–Mo–C(8)	84.3(2)
N(1)–Mo–C(9)	93.2(2)	N(2)–Mo–C(9)	91.5(2)
C(7)–Mo–C(9)	86.3(2)	C(8)–Mo–C(9)	169.0(2)
N(1)–Mo–C(10)	96.4(2)	N(2)–Mo–C(10)	173.3(2)
C(7)–Mo–C910)	88.6(2)	C(8)–Mo–C(10)	86.8(2)
C(9)–Mo–C(10)	87.3(2)	Mo–N(1)–C(11)	116.8(2)
Mo–N(1)–C(12)	108.8(2)	C(11)–N(1)–C(12)	112.1(3)
Mo–N(2)–C(13)	105.2(2)	Mo–N(2)–C(14)	112.0(3)
C(13)–N(2)–C(14)	108.7(3)	Mo–N(2)–C(15)	113.7(3)
C(13)–N(2)–C(15)	108.9(3)	C(14)–N(2)–C(15)	108.2(4)
C(2)–C(1)–C(6)	118.0(4)	C(2)–C(1)–C(11)	122.1(4)
C(6)–C(1)–C(11)	119.9(4)	C(1)–C(2)–C(3)	120.9(5)
C(2)–C(3)–C(4)	120.7(5)	C(3)–C(4)–C(5)	119.1(5)
C(4)–C(5)–C(6)	120.7(5)	C(1)–C(6)–C(5)	120.6(4)
Mo–C(7)–O(1)	179.5(3)	Mo–C(8)–O(2)	169.7(4)
Mo–C(9)–O(4)	172.7(4)	Mo–C(10)–O(3)	179.3(4)
N(1)–C(11)–C(1)	114.0(3)	N(1)–C(12)–C(13)	109.2(3)
N(2)–C(13)–C(12)	111.1(3)		

oxygen atom of another molecule is negligible in this compound though such an intermolecular bonding interaction is present in [Mo(di-2-pyridylamine)$(CO)_4$] with a shorter distance of 2.23 Å [16]. Thus, it is quite clear from both spectral and structural evidence that coordination of the nitrogen ligands can weaken an α-N–H bond more than an α-N–R bond by removing more electron density from the N–H bond than the N–R bond, explaining why the chelate-assisted oxidative addition of N–H bonds occurs more readily than N–R bonds as reported in the literature [5].

Experimental

The general operations and the spectral measurements were carried out as previously described [17]. The N–N ligands are available commercially and were used directly without further purification. Since the synthesis of [Mo(N–N)$(CO)_4$] is very straightforward, a general procedure is given below. The analytical and IR

data for these compounds are shown in Table 1 whereas the ^1H NMR data are listed in Table 2.

Preparation of [Mo(N–N)(CO)$_4$]

One millimole of N–N was added to a solution of 1 mmol of [Mo(pip)$_2$(CO)$_4$] [8] dissolved in 50 ml of CH_2Cl_2 under N_2. The solution was then heated for 20 min at 40 °C, giving a yellow-brown solution. The solvent was removed under vacuum and the product was recrystallized from MeOH/H_2O, affording orange-yellow [Mo(N–N)(CO)$_4$] (N–N = (PhCH$_2$)HNCH$_2$CH$_2$NMe$_2$, 69%; MeHNCH$_2$CH$_2$nMe$_2$, 63%; Me$_2$NCH$_2$CH$_2$NH$_2$, 56%; MeHNCH$_2$CH$_2$NHMe, 59%; and Me$_2$NCH$_2$CH$_2$CH$_2$NH$_2$, 52% yield). If freshly prepared [Mo(pip)$_2$(CO)$_4$] is used,

Table 5

Crystal data for [Mo{(PhCH$_2$)HNCH$_2$CH$_2$NMe$_2$}(CO)$_4$]

Empirical formula	$C_{15}H_{18}MoN_2O_4$
Color; habit	Orange-yellow; chunk
Crystal size	0.2 × 0.2 × 0.4 mm
Space group	*Pbca*; orthorhombic
Unit cell dimensions	$a = 14.895(7)$ Å
	$b = 11.947(4)$ Å
	$c = 19.189(8)$ Å
No. reflections for indexing	14; 6.8/27.52
Volume	3415(2) Å^3
Z	8
Formula weight	386.3
Density (calc.)	1.503 g/cm^3
Absorption coefficient	0.765 mm^{-1}
$F(000)$	1568
Diffractometer used	Siemens R3m/V
Radiation	Mo-K_α ($\lambda = 0.71073$ Å)
Temperature	297 K
Monochromator	Highly oriented graphite crystal
2θ range	2.0–50.0 °
Scan type	$\theta/2\theta$
Scan speed	Variable; 2.93–14.65 °/min in ω
Scan range (ω)	1.00 ° plus K_α-separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time
Standard reflections	3 measured every 50 reflections
Index ranges	$0 \leqslant h \leqslant 17, 0 \leqslant k \leqslant 10, 0 \leqslant l \leqslant 22$
Reflections collected	2996 ($1908 > 3.0\sigma(I)$)
Independent reflections	2600 ($1646 > 3.0\sigma(I)$)
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0002F^2$
Hydrogen atoms	Riding model, fixed isotropic U
Number of parameters refined	199
Final R indices (obs. data)	$R = 0.026$, $R_w = 0.026$
Goodness-of-fit	1.09
Largest and mean Δ/σ	0.002, 0.001
Data-to-parameter ratio	8.3:1
Largest difference peak	0.32 e Å^{-3}
Largest difference hole	−0.19 e Å^{-3}

a higher yield of $[Mo(N-N)(CO)_4]$ can be obtained; e.g., $[Mo\{(PhCH_2)HNCH_2CH_2NMe_2\}(CO)_4]$ can be obtained in a yield of 83%.

X-Ray diffraction study of $[Mo\{(PhCH_2)HNCH_2CH_2NMe_2\}(CO)_4]$

The crystals of this compound were grown from CH_2Cl_2/hexane at room temperature.

General procedures and listing of programs were previously given [18]. Absorption correction was performed on this structure using ψ scans. Final coordinates of the non-hydrogen atoms (Table 3), selected bond lengths and bond angles (Table 4), and the related crystal data (Table 5) are reported. The H-atom coordinates and structural factors are available from the authors.

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References

1 Part XV: K.-B. Shiu, K.-H. Yih, S.-L. Wang and F.-L. Liao, J. Organomet. Chem., 414 (1991) 165.
2 (a) C.A. Tolman, Chem. Rev., 77 (1977) 313; (b) J.D. Atwood, M.J. Wovkulich and D.C. Sonnenberg, Acc. Chem. Res., 16 (1983) 350; (c) M.N. Golovin, Md. M. Rahman, J. E. Belmonte and W.P. Giering, Organometallics, 4 (1985) 1981; (d) Md.M. Rahman, H.-Y. Liu, A. Prock and W.P. Giering, ibid., 6 (1987) 650; (e) Md.M. Rahman, H.-Y. Liu, K. Eriks, A Prock and W.P. Giering, ibid., (1989) 1.
3 R.T. Sanderson (Ed.), Inorganic Chemistry, Reinhold, New York, 1967, p. 105.
4 (a) S. Xiao, W.C. Trogler, D.E. Ellis and Z. Berkovitch-Yellin, J. Am. Chem. Soc., 105 (1983) 7033; (b) D.S. Marynick, ibid., 106 (1984) 4064; (c) A.G. Orpen and N.G. Connelly, J. Chem. Soc., Chem. Commun., (1985) 1310.
5 (a) D.R. Schaad and C.R. Landis, J. Am. Chem. Soc., 112 (1990) 1628; (b) F.T. Landip and J.S. Merola, Inorg. Chem., 29 (1990) 4172; (c) S. Park, M.P. Johnson and D.M. Roundhill, Organometallics, 8 (1989) 1700.
6 S. Fukuoka, M. Chono and M. Kohno, Chem. Tech., 14 (1984) 670.
7 F.A. Cotton and R.A. Walton (Eds.), Multiple Bonds between Metal Atoms, Wiley, New York, 1982, p. 26.
8 D.J. Darensbourg and R.L. Kump, Inorg. Chem., 17 (1978) 2680.
9 (a) C.M. Lukehart (Ed.), Fundamental Transition Metal Organometallic Chemistry, Wadsworth, 1985, p. 80; (b) K.-B. Shiu and C.-J. Chang, J. Chin. Chem. Soc. (Taipei), 34 (1987) 297.
10 (a) R.S. Drago (Ed.), Physical Methods in Chemistry, Saunders, Philadelphia, PA, 1977, Chap. 6; (b) E.A.V. Ebsworth, D.W.H. Rankin and S. Cradock (Eds.), Structural Methods in Inorganic Chemistry, Blackwell Scientific, Oxford, 1986, Chap. 5.
11 W. Strohmeier and F.J. Muller, Chem. Ber., 100 (1967) 2812.
12 C.A. Tolman, J. Am. Chem. Soc., 92 (1970) 2953, 2956.
13 (a) C.S. Kraihanzel and F.A. Cotton, Inorg. Chem., 2 (1963) 533; (b) R. Poilblanc and M. Bigorgne, J. Organomet. Chem., 5 (1966) 93.
14 (a) J.E. Huheey, J. Org. Chem., 36 (1971) 204; (b) J.F. Sebastian, J. Chem. Educ., 48 (1971) 97.
15 L. Libit and R. Hoffmann, J. Am. Chem. Soc., 96 (1974) 1370.
16 R.A. Howie, G. Izquierdo and G.P. McQuillan, Inorg. Chem. Acta, 72 (1983) 165.
17 (a) K.-B. Shiu and L.-Y. Lee, J. Organomet. Chem., 348 (1988) 357; (b) K.-B. Shiu, K.-S. Liou, C.P. Cheng, B.-R. Fang, Y. Wang, G.-H. Lee and W.-J. Vong, Organometallics, 8 (1989) 1219.
18 K.-B. Shiu, F.-M. Shen, S.-L. Wang and S.-C. Wei, J. Organomet. Chem., 372 (1989) 251.