Journal of Organometallic Chemistry, 453 (1993) 201–206

JOM 23464

Coordination characteristics of three N,N′-di(azol-1-yl)methanes; substituent effects on infrared absorption and structure of the Group VI metal carbonyl derivatives *

Kom-Bei Shiu and Kuen-Song Liou

Department of Chemistry, National Cheng Kung University, Tainan 70101 (Taiwan)

Yu Wang, Ming-Chu Cheng and Gene-Hsiang Lee

Department of Chemistry, National Taiwan University, Taipei 10764 (Taiwan)

(Received October 17, 1992; in revised form December 11, 1992)

Abstract

Compounds $[M(H_2CAz_2)(CO)_4]$ (M = Cr, Mo, or W), were obtained readily and similarly by refluxing the equivalent amounts of N,N′-di(azol-1-yl)methanes, H_2CAz_2 (Az = pyrazol-1-yl (Pz), 3,5-dimethylpyrazol-1-yl (Pz′) or 3,4,5-trimethylpyrazol-1-yl (Pz″) with $[M(CO)_6]$ (M = Cr, Mo, or W) in a mixed solvent system of 1,2-dimethoxyethane and tetrahydrofuran. Under phase transfer catalysis conditions this gives rise to the new nitrogen-bidentate ligand, $H_2CPz''_2$, by reaction of HPz″ with methylene chloride. IR absorption bands in the carbonyl region indicate that no regular trends can be found for different substituents on the pyrazolyl ring. This irregularity is attributed to flexibility of the boat conformation formed from the metal centre and the ligand, which is supported by comparative structure details of $[Mo(H_2CPz'_2)(CO)_4]$, reported previously, $[W(H_2CPz''_2)(CO)_4]$ (**6**) and $[W(H_2CPz'_2)(CO)_4]$ (**7**): **6**, triclinic, $P\bar{1}$, $a = 8.403(3)$, $b = 9.589(3)$, $c = 13.310(3)$ Å, $\alpha = 94.476(22)$, $\beta = 102.837(21)$, $\gamma = 110.355(25)°$, $Z = 2$, $R = 0.024$, $R_w = 0.023$, based on 3070 with $I > 2\sigma(I)$. **7**, monoclinic, $P2_1/c$, $a = 9.178(3)$, $b = 15.885(9)$, $c = 12.394(10)$ Å, $\beta = 108.64(9)°$, $Z = 4$, $R = 0.030$, $R_w = 0.030$, based on 2625 reflections with $I > 2.5\sigma(I)$.

1. Introduction

The syntheses and applications of neutral poly(azol-1-yl)alkanes, $R_nC(Az)_{4-n}$ (R = H, alkyl, or aryl; HAz = di-, tri- or tetra-azole; $n = 2$, 3, or 4), as multidentate ligands with either main-group or transition-metal atoms have been extensively studied [1–4]. Especially recently, ligands with Az = pyrazol-1-yl (Pz) or 3,5-dimethylpyrazol-1-yl (Pz′) have been the most vigorously developed. From the literature, it appears obvious, as one would expect, that ligands with more methyl-group substituents should have greater electron-donating ability, a feature previously reported for 1,10-phenanthroline (phen) (or 2,2′-bipyridine (bpy)) and the relevant substituted derivatives [5]. However, we wish to present IR evidence that no regular trends are in fact observable for $[Cr(H_2CAz_2)(CO)_4]$, $[Mo(H_2CAz_2)i(CO)_4]$, or $[W(H_2CAz_2)(CO)_4]$. This unexpected irregularity can be rationalized by comparing the structural details of $[Mo(H_2CPz'_2)(CO)_4]$, reported in 1989 [6], $W(H_2CPz'_2)(CO)_4]$ and $[W(H_2CPz''_2)(CO)_4]$, where Pz″ is 3,4,5-trimethylpyrazol-1-yl (Fig. 1).

2. Experimental section

All operations were performed by the usual Schlenk techniques [7], using deoxygenated, dry solvents and gases. IR spectra, calibrated with polystyrene, were recorded on a Hitachi Model 260-30 instrument. Abbreviations are as follows: vs, very strong; s, strong; m, medium and sh, shoulder. NMR spectra were obtained on a Bruker WP-100 (^1H, 100 MHz) FT-NMR spectrometer. Chemical shifts (δ in ppm, J in herz) are

---

Correspondence to: Dr. K.-B. Shiu.

* Part of synthetic result is taken from K.-S. Liou, *M. Sc. Thesis*, National Cheng Kung University, Tainan, 1988.

0022-328X/93/$6.00

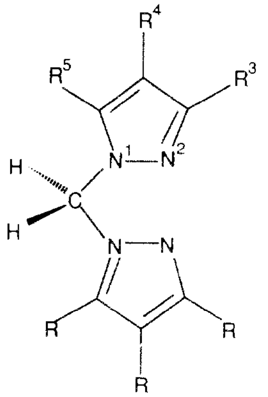

Fig. 1. Structure and numbering scheme for H_2CAz_2 ligands: (i) 3-C-R = 4-C-R = 5-C-R = H; H_2CAz_2 = H_2CPz_2. (ii) 3-C-R = 5-C-R = Me, 4-C-R = H: H_2CAz_2 = $H_2CPz'_2$. (iii) 3-C-R = 4-C-R = 5-C-R = Me: H_2CAz_2 = $H_2CPz''_2$.

defined as positive downfield or negative upfield relative to internal $SiMe_4$ (TMS) standard; abbreviations are s, singlet; d, doublet; br, unresolved multiplet or two overlapped singlets. Elemental analysis was performed by the Microanalytical Service of the Department of Chemistry, National Cheng Kung University. Melting points were determined with a Mel-Temp apparatus (Laboratory Devices) and are not corrected.

3,4,5-Trimethylpyrazole (HPz'') was prepared from 3-methylpentane-2,4-dione [8] by following Vogel's procedure [9]. HPz'', a white solid with a typical yield of 78%, mp. 139–140°C. Anal. Found: C, 65.53; H, 9.18; N, 25.18. $C_6H_{10}N_2$ calc.: C, 65.43; H, 9.15; N, 25.42%. ^{1}H NMR (23°C, $CDCl_3$, 100 MHz): 3- and 5-methyl groups, δ 2.18 (6H, s); 4-methyl group, 1.89 (3H, s); N–H, 11.11 (1H, s)). The ligand $H_2CPz''_2$ was then prepared with the same procedure as for $H_2CPz'_2$ [3]: $H_2CPz''_2$, a white floppy solid, yield 85%, mp. 146–147°C. Anal. Found: C, 66.98; H, 8.60; N, 24.13. $C_{13}H_{20}N_4$ calc.: C, 67.20; H, 8.68; N, 24.12%. ^{1}H NMR (23°C, $CDCl_3$, 100 MHz): 3- and 5-methyl groups, δ 2.12 (6H, s), 2.32 (6H, s); 4-methyl group, 1.64 (6H, s); CH_2, 6.04 (2H, br).

2.1. Preparation of [$Cr(H_2CPz_2)(CO)_4$] (1)

A mixture of H_2CPz_2 (0.74 g, 5.00 mmol), prepared from HPz (Aldrich) by the literature procedure [3], and [$Cr(CO)_6$] (1.10 g, 5.00 mmol) in 40 ml of 1,2-dimethoxyethane (DME) and 10 ml of tetrahydrofuran (THF) was refluxed for 24 h. The solvents were then removed under vacuum. Recrystallization from acetone/MeOH gave the yellow product (1.36 g, 87%). Anal. Found: C, 42.30; H, 2.65; N, 17.95. $C_{11}H_8CrN_4O_4$ calc.: C, 42.32; H, 2.58; N, 17.95%. ^{1}H NMR (23°C, acetone-d_6, 100 MHz): hydrogen atoms on the ring-3 and -5 positions, δ 8.14 (2H, d, ^3J(H,H) = 2.4), 8.00 (2H, d, ^3J(H,H) = 1.9); hydrogen atoms on the ring-4 position, 6.48 (2H, t); CH_2, 6.64 (2H, br). IR (CH_2Cl_2): ν(CO), 2006m, 1890vs, 1872sh, 1832s and IR (KBr): ν(CO), 2007s, 1897sh, 1874vs, 1802s cm^{-1}.

2.2. Preparation of [$Mo(H_2CPz_2)(CO)_4$] (2)

This milky yellow compound was obtained in 85% yield by an analogous procedure (*ca.* 3 h). Anal. Found: C, 36.89; H, 2.23; N, 15.68. $C_{11}H_8MoN_4O_4$ calc.: C, 37.10; H, 2.26; N, 15.74%. ^{1}H NMR (23°C, $CDCl_3$, 100 MHz): hydrogen atoms on the ring-3 and -5 positions, δ 8.17 (2H, d, ^3J(H,H) = 2.2), 7.96 (2H, d, ^3J(H,H) = 1.9); hydrogen atoms on the ring-4 position, 6.48 (2H, t); CH_2, 6.74 (2H, br). IR (MeCN): ν(CO), 2014m, 1896vs, 1875sh, 1837s and IR (KBr): ν(CO), 2011s, 1915sh, 1872vs, 1805s cm^{-1}.

2.3. Preparation of [$W(H_2CPz_2)(CO)_4$] (3)

This yellow compound was obtained in 78% yield by an analogous procedure (*ca.* 24 h). Anal. Found: C, 29.71; H, 1.88; N, 12.64. $C_{11}H_8N_4O_4W$ calc.: C, 29.75; H, 1.82; N, 12.62%. ^{1}H NMR (23°C, $CDCl_3$, 100 MHz): hydrogen atoms on the ring-3 and -5 positions, δ 8.22 (2H, d, ^3J(H,H) = 2.3), 8.09 (2H, d, ^3J(H,H) = 2.1); hydrogen atoms on the ring-4 position, 6.53 (2H, t); CH_2, 6.80 (2H, br). IR (MeCN): ν(CO), 2004m, 1879vs, 1827s and IR (KBr): ν(CO), 2004s, 1897sh, 1862vs, 1792s cm^{-1}.

2.4. Preparation of [$Cr(H_2CPz''_2)(CO)_4$] (4)

This compound was obtained in 78% yield by an analogous procedure (*ca.* 24 h) from a mixture of (0.27 g, 2.00 mmol) and [$Cr(CO)_6$] (0.44 g, 2.00 mmol) in 40 ml of DME and 10 ml of THF. Recrystallization from CH_2Cl_2/MeOH gave the pale orange-yellow product (0.64 g, 81%). Anal. Found: C, 51.36; H, 5.12; N, 14.23. $C_{17}H_{20}CrN_4O_4$ calc.: C, 51.51; H, 5.09; N, 14.14%. ^{1}H NMR (23°C, $CDCl_3$, 100 MHz): 3- and 5-methyl groups, δ 2.27 (6H, s), 2.45 (6H, s); 4-methyl group, 1.88 (6H, s); CH_2, 6.12 (2H, br). IR (CH_2Cl_2): ν(CO), 2004m, 1884vs, 1869sh, 1827s and IR (KBr): ν(CO), 2003s, 1884sh, 1867vs, 1817s cm^{-1}.

2.5. Preparation of [$Mo(H_2CPz''_2)(CO)_4$] (5)

This pale yellow compound was obtained in 85% yield by an analogous procedure (*ca.* 2.5 h). Anal. Found: C, 46.21; H, 4.55; N, 12.70. $C_{17}H_{20}MoN_4O_4$ calc.: C, 46.37; H, 4.58; N, 12.73%. ^{1}H NMR (23°C, $CDCl_3$, 100 MHz): 3- and 5-methyl groups, δ 2.30 (6H, s), 2.39 (6H, s); 4-methyl group, 1.89 (6H, s); CH_2, 6.32 (1H, s), 6.06 (1H, s). IR (CH_2Cl_2): ν(CO) 2014m, 1895vs, 1874sh, 1832s and IR (KBr): ν(CO), 2011s, 1900sh, 1870vs, 1819s cm^{-1}.

2.6. *Preparation of $[W(H_2CPz''_2)(CO)_4]$ (6)*

This yellow compound was obtained in 83% yield by an analogous procedure (*ca.* 24 h). Anal. Found: C, 38.44; H, 3.81; N, 10.48. $C_{17}H_{20}N_4O_4W$ calc.: C, 38.65; H, 3.82; N, 10.61%. ^1H NMR (23°C, $CDCl_3$, 100 MHz): 3- and 5-methyl groups, δ 2.31 (6H, s), 2.40 (6H, s); 4-methyl group, 1.90 (6H, s); CH_2, 6.31 (1H, s), 6.06 (1H, s). IR (CH_2Cl_2): ν(CO), 2003m, 1877vs, 1867sh, 1822s and IR (KBr): ν(CO), 1995s, 1874sh, 1857vs, 1810s cm^{-1}.

2.7. *X-Ray diffraction study of $[W(H_2CPz''_2)(CO)_4]$ (6) and $[W(H_2CPz'_2)(CO)_4]$ (7)*

Crystals of **6** and **7** were grown from CH_2Cl_2/hexane at room temperature. General procedures and listings of programs were given previously [6]. Absorption correction was performed on both structures using ψ scans. Related crystal data (Table 1), final coordinates of the non-hydrogen atoms (Table 2), and selected bond lengths and bond angles (Table 3) are reported. The anisotropic displacement coefficients of the atoms, the H-atom coordinates and structural factors are available from the authors. The ORTEP plots for **6** and **7** with the relevant numbering scheme are drawn in Figs. 2 and 3, respectively.

3. Results and discussion

We have prepared $[M(H_2CPz_2)(CO)_4]$ and $[M(H_2CPz''_2)(CO)_4]$ (M = Cr, Mo, or W) under similar reaction conditions to those used for $[M(H_2CPz'_2)(CO)_4]$ [10]. These compounds are well characterized as *cis*-$[M(\eta^2\text{-}(H_2CAz_2))(CO)_4]$ by elemental analysis, IR and NMR spectral results. Since the IR data of $[M(H_2CPz_2)(CO)_4]$ are quite similar to those reported previously by Lobia and Bonati [4], it is thus clear that our reaction condition can apply in the synthesis of the metal carbonyl derivatives of all three types of H_2Az_2, whether the substituents on the pyrazolyl ring are hydrogen atoms or methyl groups (the condition Lobia and Bonati used [4] applied only for $H_2CAz_2 = H_2CPz_2$.)

TABLE 1. Crystal data for **6** and **7**

Compound	**6**	**7**
Empirical formula	$C_{17}H_{20}N_4O_4W$	$C_{15}H_{16}N_4O_4W$
Colour	yellow	yellow
Crystal size (mm)	0.30 × 0.36 × 0.42	0.40 × 0.30 × 0.30
Space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$
Unit cell dimensions		
a, *b*, *c*, Å	8.403(3), 9.589(3), 13.310(3)	9.178(3), 15.885(9), 12.394(10)
α, β, γ, deg	94.476(22), 102.837(21), 110.355(25)	90, 108.68(4), 90
Volume, $Å^3$	966.0(5)	1711.8(17)
Z	2	4
Formula weight	528.21	500.16
D_{calc}, g/cm^3	1.816	1.941
h, *k*, *l* ranges	−9 to 9, 0 to 11, −15 to 15	−10 to 10, 0 to 18, 0 to 14
Abs cor	ψ scan	
Abs coeff, mm^{-1}	6.13	1.94
Transm range	0.4799–0.9995	0.5436–0.9984
F(000)	511.83	951.66
Diffractometer used	Nonius CAD4	
Radiation; λ, Å	Mo Kα; 0.70930	
Temperature (K)	297	
Scan type	$\theta/2\theta$	
2θ range, deg	2–50	
Scan speed, deg/min	1.43–10	1.66–10
Std rflns	3 std/7200 sec	
Decay; %	≤ 1	≤ 1
No. of unique rflns	3403	2992
No. of rflns (N_o) used	3070 with $I > 2.0\sigma(I)$	2625 with $I > 2.5\sigma(I)$
No. of atoms refined	46	40
No. of params (N_v) refined	236	218
Max Δ/σ ratio	0.347	0.012
R; R_w S [a]	0.024, 0.023, 2.77	0.030, 0.030, 4.54
Resid peak; hole $e/Å^3$	0.96, −0.96	0.94, −1.60 [b]

[a] $S = [\Sigma_w |F_o - F_c|^2/(N_o - N_v)]^{1/2}$, $w^{-1} = \sigma^2(F_o)$, [b] ghost peaks.

TABLE 2. Fractional atomic coordinates and B_{iso} [a] for **6** and **7**

	x	y	z	B_{iso}
*(a) Compound **6***				
W	0.99397(3)	0.712160(24)	0.271358(16)	2.922(11)
C1	0.8986(7)	0.7500(6)	0.3913(4)	3.5(3)
C2	1.0809(8)	0.5843(6)	0.3547(4)	4.2(3)
C3	0.7774(8)	0.5386(7)	0.2179(4)	4.5(3)
C4	1.0909(9)	0.6439(6)	0.1596(4)	4.4(4)
C5	1.4110(7)	0.9530(7)	0.3420(4)	3.8(3)
C6	1.5108(7)	1.1072(7)	0.3612(4)	3.9(3)
C7	1.3932(7)	1.1775(6)	0.3533(4)	3.6(3)
C8	1.0613(7)	1.0788(5)	0.3119(4)	3.0(3)
C9	0.8000(7)	0.8408(6)	0.0747(4)	3.4(3)
C10	0.7939(7)	0.9763(6)	0.0463(4)	3.3(3)
C11	0.8932(7)	1.0848(6)	0.1307(4)	3.4(3)
C12	1.4788(8)	0.8293(8)	0.3427(5)	5.4(4)
C13	1.7067(8)	1.1797(8)	0.3882(5)	6.2(4)
C14	1.4211(8)	1.3411(7)	0.3664(5)	5.3(4)
C15	0.7122(9)	0.6866(7)	0.0104(4)	5.8(4)
C16	0.6984(9)	0.9947(7)	−0.0575(4)	5.0(4)
C17	0.9330(10)	1.2490(7)	0.1450(5)	5.9(5)
N1	1.2399(6)	0.9256(5)	0.3225(3)	3.22(23)
N2	1.2309(6)	1.0679(5)	0.3299(3)	3.04(21)
N3	0.9557(5)	1.0172(4)	0.2058(3)	2.88(21)
N4	0.8985(6)	0.8647(5)	0.1728(3)	3.10(21)
O1	0.8406(6)	0.7585(5)	0.4609(3)	5.7(3)
O2	1.1288(6)	0.5016(5)	0.4017(3)	6.3(3)
O3	0.6501(6)	0.4274(5)	0.1892(4)	6.5(3)
O4	1.1494(7)	0.5957(5)	0.1010(3)	6.6(3)
*(b) Compound **7***				
W	0.96959(4)	0.098930(17)	0.284295(24)	2.452(11)
N1	0.7589(7)	0.0450(3)	0.3142(4)	2.5(3)
N2	0.8590(7)	0.0277(3)	0.1196(4)	2.7(3)
N3	0.7139(7)	−0.0369(3)	0.2865(5)	2.8(3)
N4	0.7822(7)	−0.0462(3)	0.1186(4)	2.8(3)
C	0.7915(9)	−0.0863(4)	0.2241(6)	3.1(4)
C1	1.1461(10)	0.1482(4)	0.2547(6)	3.9(4)
O1	1.2548(7)	0.1830(4)	0.2455(5)	5.5(3)
C2	1.1148(9)	0.0027(4)	0.3495(6)	3.0(3)
O2	1.2110(7)	−0.0451(3)	0.3865(5)	4.9(3)
C3	0.8656(10)	0.2103(4)	0.2238(6)	3.7(4)
O3	0.8279(8)	0.2762(3)	0.1930(5)	6.6(4)
C4	1.0469(10)	0.1505(4)	0.4363(6)	4.0(5)
O4	1.0937(7)	0.1792(3)	0.5245(4)	5.8(4)
C11	0.6617(9)	0.1628(4)	0.3988(6)	3.6(4)
C12	0.6561(9)	0.0773(4)	0.3587(5)	2.7(3)
C13	0.5471(9)	0.0154(4)	0.3601(6)	3.3(4)
C14	0.5874(9)	−0.0563(4)	0.3142(6)	3.0(3)
C15	0.5155(10)	−0.1422(5)	0.2955(7)	4.8(5)
C21	0.8939(11)	0.1254(5)	−0.0264(6)	4.6(5)
C22	0.8279(9)	0.0489(5)	0.0093(6)	3.3(4)
C23	0.7321(10)	−0.011(5)	−0.0605(6)	4.1(4)
C24	0.7027(10)	−0.0694(5)	0.0100(7)	4.2(4)
C25	0.6045(13)	−0.1463(6)	−0.0185(7)	6.3(6)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

In the literature, numerous *cis*-disubstituted tetracarbonyl complexes of the group VI metal atoms, $[M(L\text{-}L)(CO)_4]$, are known [11]. The four carbonyl stretching bands (*i.e.*, four IR-active vibrations), which are usually displayed in these compounds have been assigned by Cotton and Kraihanzel on the basis of a simple group theory analysis [12]; two vibrations associated with the *trans*-carbonyl groups (assigned as $A_1\ CO^{(1)}$ and $B_2\ CO^{(1)}$) occur at 1869 and 1825 cm^{-1} and two other vibrations associated with the *cis*-carbonyl ligands (assigned as $A_1\ CO^{(2)}$ and $B_1\ CO^{(2)}$) occur at the higher wavenumbers of 2009 and 1897 cm^{-1} in CH_2Cl_2 for L-L = bpy. By comparing either only one or all ν(CO) values of $[M(L\text{-}L)(CO)_4]$ [11] or [*cis*-$M(L\text{-}L)_2(CO)_2$] [13], one can deduce the relative π-acceptor ability of chelating ligands. L-L, giving an order such as bpy < phen < dmpe < dppm < dppe < PF_3 (two PF_3 ligands take the place of one chelate), where dmpe is 1,2-bis(dimethylphosphino)ethane; dppm is bis(diphenylphosphino)-methane and dppe is 1,2-bis(diphenylphosphino)ethane. Since the ligands we used are also symmetrical like dppm or bpy, we first list the ν(CO) values for $[M(H_2CAz_2)(CO)_4]$ (M = Cr, Mo, or W; Az = Pz, Pz′, or Pz″) (Table 4) and then compare one or all ν(CO) bands in the hope that effects of different substituents would be reflected in the values, a feature previously reported for phen (or bpy) and the relevant substituted derivatives [5]. In fact, as observed from these values, no regular trend for $[Cr(H_2CAz_2)(CO)_4]$, $[Mo(H_2CAz_2)(CO)_4]$, or $[W(H_2CAz_2)(CO)_4]$, can be inferred taking account of experimental error, although one can conclude that the ν(CO) values of $[Mo(H_2CAz_2)(CO)_4]$ are similar to those of $[Mo(bpy)(CO)_4]$ and the π-acceptor ability of H_2CAz_2 is similar to that of bpy (previously, Oro *et al.* suggested the similarity in π-acid ability between H_2CPz_2 and bpy on the basis of comparing the ν(CO) values of $[Rh(L\text{-}L)(CO)_2]ClO_4$ [14]). Quite obviously, when the substituents on the pyrazolyl rings are changed, the donor ability of the ligand is different from what would be expected. Since donor ability can be inferred from related structures, we decided to characterize at least two compounds with different substituents by X-ray crystallography and compare related structural features.

From Figs. 2 and 3 and Table 2, one can observe clearly that structures of both $[W(H_2CPz''_2)(CO)_4]$ (**6**) and $[W(H_2CPz'_2)(CO)_4]$ (**7**) are very similar to that of $[Mo(H_2CPz'_2)(CO)_4]$ (**8**) [6], in having a six-membered boat metallacycle, formed from H_2CAz_2 and the metal atom, and two distorted *cis*-carbonyls. However, if four different planes are defined and calculated for **6**–**8**, including two pyrazolyl-ring planes and two other ones (for example, W, N(1), N(4) in one plane and C(8), N(2), N(3) in the other in **6** (Fig. 2)), different structural features resulting from the methyl-group substitution can be recognized evidently. These two planes form an angle of 82.9° in **6**, 85.0° in **7**, and 86.1° in **8** while the two pyrazolyl-ring planes form an angle of

TABLE 3. Selected bond lengths (Å) and angles (°) for **6** and **7**

*(a) Compound **6***			
(i) Bond lengths			
W–C(1)	2.000(6)	C(6)–C(13)	1.491(8)
w–C(2)	1.935(5)	C(7)–C(14)	1.493(8)
W–C(3)	1.929(7)	C(7)–N(2)	1.351(7)
W–C(4)	2.015(6)	C(8)–N(2)	1.434(7)
W–N(1)	2.267(4)	C(8)–N(3)	1.441(6)
W–N(4)	2.270(4)	C(9)–C(10)	1.395(7)
C(1)–O(1)	1.149(7)	C(9)–C(15)	1.492(8)
C(2)–O(2)	1.170(7)	C(9)–N(4)	1.335(6)
C(3)–O(3)	1.178(8)	C(10)–C(11)	1.356(8)
C(4)–O(4)	1.157(7)	C(10)–C(16)	1.493(7)
C(5)–C(6)	1.393(9)	C(11)–C(17)	1.479(8)
C(5)–C(12)	1.484(8)	C(11)–N(3)	1.342(6)
C(5)–N(1)	1.328(7)	N(1)–N(2)	1.390(6)
C(6)–C(7)	1.368(8)	N(3)–N(4)	1.370(6)
(ii) Bond angles			
C(1)–W–C(2)	84.57(22)	C(6)–C(7)–C(14)	131.0(5)
C(1)–W–C(3)	86.57(24)	C(6)–C(7)–N(2)	106.9(5)
C(1)–W–C(4)	170.80(21)	C(14)–C(7)–N(2)	122.1(5)
C(1)–W–N(1)	95.11(19)	N(2)–C(8)–N(3)	112.4(4)
C(1)–W–N(4)	96.38(18)	C(10)–C(9)–C(15)	127.9(5)
C(2)–W–C(3)	86.78(25)	C(10)–C(9)–N(4)	110.4(5)
C(2)–W–C(4)	86.83(22)	C(15)–C(9)–N(4)	121.7(5)
C(2)–W–N(1)	98.08(21)	C(9)–C(10)–C(11)	106.1(4)
C(2)–W–N(4)	178.61(21)	C(9)–C(10)–C(16)	125.9(5)
C(3)–W–C(4)	89.71(25)	C(11)–C(10)–C(16)	128.0(5)
C(3)–W–N(1)	174.99(19)	C(10)–C(11)–C(17)	129.7(5)
C(3)–W–N(4)	94.28(20)	C(10)–C(11)–N(3)	107.4(4)
C(4)–W–N(1)	89.31(20)	C(17)–C(11)–N(3)	122.9(5)
C(4)–W–N(4)	92.28(18)	W–N(1)–C(5)	133.7(4)
N(1)–W–N(4)	80.85(15)	W–N(1)–N(2)	121.7(3)
W–C(1)–O(1)	173.9(5)	C(5)–N(1)–N(2)	104.3(4)
W–C(2)–O(2)	177.1(5)	C(7)–N(2)–C(8)	130.1(4)
W–C(3)–O(3)	175.7(5)	C(7)–N(2)–N(1)	111.2(4)
W–C(4)–O(4)	173.9(5)	C(8)–N(2)–N(1)	118.7(4)
W(6)–C(5)–C(12)	126.6(5)	C(8)–N(3)–C(11)	130.2(4)
C(6)–C(5)–N(1)	111.6(5)	C(8)–N(3)–N(4)	118.5(4)
C(12)–C(5)–N(1)	121.8(5)	C(11)–N(3)–N(4)	111.2(4)
C(5)–C(6)–C(7)	106.1(5)	W–N(4)–C(9)	132.5(3)
C(5)–C(6)–C(13)	126.5(6)	W–N(4)–N(3)	122.2(3)
C(7)–C(6)–C(13)	127.4(6)	C(9)–N(4)–N(3)	104.9(4)
(b) Compound 7			
(i) Bond lengths			
W–N(1)	2.252(6)	N(4)–C(24)	1.360(9)
W–N(2)	2.270(5)	C(1)–O(1)	1.178(10)
W–C(1)	1.937(8)	C(2)–O(2)	1.144(9)
W–C(2)	2.018(7)	C(3)–O(3)	1.131(9)
W–C(3)	2.036(7)	C(4)–O(4)	1.134(9)
W–C(4)	1.966(7)	C(11)–C(12)	1.442(9)
N(1)–N(3)	1.375(7)	C(12)–C(13)	1.407(10)
N(1)–C(12)	1.339(9)	C(13)–C(14)	1.375(10)
N(2)–N(4)	1.367(8)	C(14)–C(15)	1.502(10)
N(2)–C(22)	1.347(9)	C(21)–C(22)	1.486(11)
N(3)–C	1.441(9)	C(22)–C(23)	1.394(11)
N(3)–C(14)	1.347(9)	C(23)–C(24)	1.359(11)
N(4)–C	1.432(9)	C(24)–C(25)	1.492(12)
(ii) Bond angles			
N(1)–W–N(2)	78.35(19)	C–N(3)–C(14)	128.8(6)
N(1)–W–C(1)	177.9(3)	N(2)–N(4)–C	119.6(5)
N(1)–W–C(2)	97.91(24)	N(2)–N(4)–C(24)	110.7(5)
N(1)–W–C(3)	93.7(3)	C–N(4)–C(24)	129.7(6)
N(1)–W–C(4)	93.8(3)	N(3)–C–N(4)	110.7(5)
N(2)–W–C(1)	101.1(3)	W–C(1)–O(1)	173.7(6)
N(2)–W–C(2)	91.75(24)	W–C(2)–O(2)	171.7(6)
N(2)–W–C(3)	94.6(3)	W–C(3)–O(3)	170.4(7)
N(2)–W–C(4)	171.7(3)	W–C(4)–O(4)	178.7(7)
C(1)–W–C(2)	84.1(3)	N(1)–C(12)–C(11)	123.5(6)
C(1)–W–C(3)	84.3(3)	N(1)–C(12)–C(13)	109.5(6)
C(1)–W–C(4)	86.9(3)	C(11)–C(12)–C(13)	127.0(7)
C(2)–W–C(3)	167.7(3)	C(12)–C(13)–C(14)	106.7(6)
C(2)–W–C(4)	86.7(3)	N(3)–C(14)–C(13)	106.5(6)
C(3)–W–C(4)	88.5(3)	N(3)–C(14)–C(15)	122.7(6)
W–N(1)–N(3)	121.6(4)	C(13)–C(14)–C(15)	130.8(7)
W–N(1)–C(12)	132.7(4)	N(2)–C(22)–C(21)	122.2(7)
N(3)–N(1)–C(12)	105.7(5)	N(2)–C(22)–C(23)	110.2(6)
W–N(2)–N(4)	121.1(4)	C(21)–C(22)–C(23)	127.6(7)
W–N(2)–C(22)	132.5(5)	C(22)–C(23)–C(24)	106.4(6)
N(4)–N(2)–C(22)	105.4(5)	N(4)–C(24)–C(23)	107.3(7)
N(1)–N(3)–C	119.3(5)	N(4)–C(24)–C(25)	123.3(7)
N(1)–N(3)–C(14)	111.5(5)	C(23)–C(24)–C(25)	129.4(7)

120.8° in **6**, 68.2° in **7** and 68.1° in **8**. Apparently, the boat conformation does not change much whether the central metal atom is tungsten or molybdenum. This feature is to be expected from the similarity in the radii of the two atoms because of the lanthanide contraction [15]. However, when the hydrogen atom on the ring-4 position of Pz′ is replaced by a methyl group, the conformation changed greatly as observed in various angles for **6**. We found that the net result from this conformational modification is best exemplified by one angle, formed by two *cis*-carbonyl groups and the central metal atom, which is 170.80(21)° in **6**, 167.7(3)° in **7**, or 167.3(1)° in **8**. As observed in Table 3, either boat conformation resulting from different substituents has

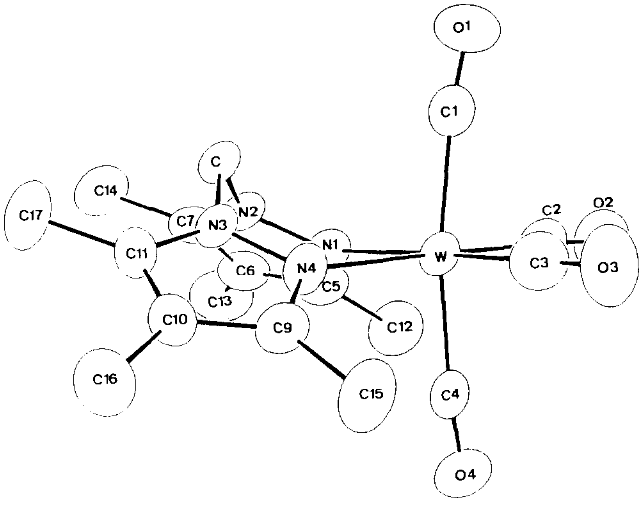

Fig. 2. ORTEP drawing of $[W\{\eta^2\text{-}(H_2CPz''_2)\}(CO)_4]$ (**6**) with the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

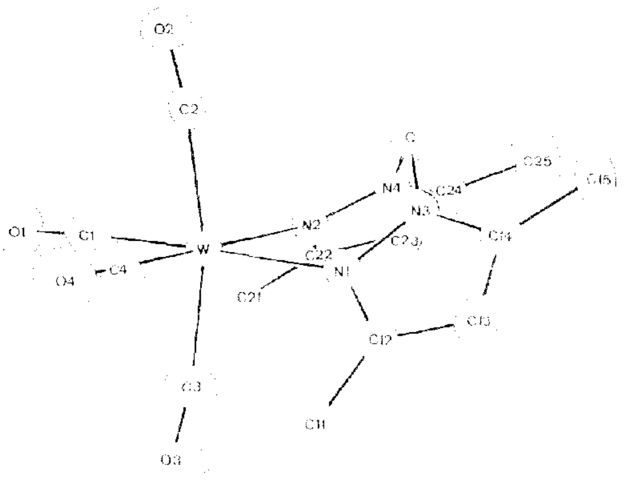

Fig. 3. ORTEP drawing of $[W\{\eta^2\text{-}(H_2CPz'_2)\}(CO)_4]$ (7) with the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

caused some bond angles, especially those formed by carbonyls in the molecule, at the corresponding locations to differ significantly from each other; for example, C(3)–W–C(4) 89.71(25)° in **6** and C(3)–W–C(1) 84.3(3)° in **7** (*cf.* Figs. 2 and 3), and influences (probably in a complicated way) the relevant carbonyl stretching frequencies so that no simple trend in the ν(CO) values can be found. How can we explain the structural change observed as more substituents are added? Constructing a model shows clearly that nonbonded repulsive interactions exist between the substituents especially at the ring-3 (and ring-5) positions of two pyrazolyl rings as well as interactions between the substituents at the ring-3 (or ring-5) and at the ring-4 positions of the same pyrazolyl ring. Hence, when the replacement by methyl groups of the hydrogen atoms at the ring-4 positions of $H_2CPz'_2$ occurs, repulsive interactions increase, creating a poorer environment for the nonbonded interactions between two methyl groups at the ring-3 (or ring-5) positions of two different pyrazolyl rings in $H_2CPz''_2$, as indicated by the large angle (120.8°) in **6**, formed by two pyrazolyl-ring planes compared with those of 68.2° in **7** and 68.1° in **8**.

TABLE 4. Carbonyl stretching frequencies for $[M(H_2CAz_2)(CO)_4]$ [a]

M	Az	A_1	B_1	A_1	B_2
Cr	Pz	2006	1890	1872	1832
Cr	Pz'	2000	1887	1867	1830
Cr	Pz''	2004	1884	1869	1827
Mo	Pz	2014	1896	1875	1837
Mo	Pz'	2006	1893	1872	1834
Mo	Pz''	2014	1895	1874	1832
W	Pz	2004	1879	— [b]	1827
W	Pz'	2003	1877	1862	1828
W	Pz''	2003	1877	1867	1822

[a] IR spectra of $[Mo(H_2CPz_2)(CO)_4]$ and $[W(H_2CPz_2)(CO)_4]$ were measured in MeCN. Those of all other complexes were measured in CH_2Cl_2. [b] see text.

In conclusion, the flexibility of the boat six-membered metallacycle allows adjustment of the chelate structure to minimize the nonbonded repulsive interactions. The structural modification then alters the electron donating ability so that no regular trend in carbonyl stretching values for $[M(H_2CAz_2)(CO)_4]$ is observed: as more replacement of hydrogen atoms by methyl-group substituents takes place on the pyrazolyl ring, the electron donating ability of the resulting ligand, H_2CAz_2 (Fig. 1), does not become necessarily stronger as would have been expected.

Acknowledgment

We wish to thank the National Science Council of the Republic of China for financial support of this research (Contract No. NSC82-0208-M006-32).

References

1 (a) S. Trofimenko, *Chem. Rev.*, 72 (1972) 497; (b) S. Trofimenko, *Prog. Inorg. Chem.*, 34 (1986) 115.
2 A.R. Katritzky, A.E. Abdel-Rahman, D.E. Leahy and O.A. Schwarz, *Tetrahedron*, 39 (1983) 4133.
3 S. Julia, P. Sala, J. del Mazo, M. Sancho, C. Ochoa, J. Elguero, J.-P. Fayet and M.-C. Vertut, *J. Heterocycl. Chem.*, 19 (1982) 1141.
4 G.G. Lobbia and F. Bonati, *J. Organomet. Chem.*, 366 (1989) 121 and references cited therein.
5 (a) G. Ciani, G. Zassinovich and G. Mestroni, *Inorg. Chim. Acta*, 112 (1986) 103; (b) J.A. Connor and C. Overton, *J. Organomet. Chem.*, 249 (1983) 165.
6 K.-B. Shiu, C.-J. Chang, Y. Wang and M.-C. Cheng, *J. Chin. Chem. Soc. (Taipei)*, 36 (1989) 25.
7 D.F. Shriver (Ed.), *Manipulation of Air Sensitive Compounds*, McGraw-Hill, New York, 1969.
8 H.E. Baumgarten, *Org. Syntheses, Collective Vol. 5*, p. 785.
9 B.S. Furniss, A.J. Hannaford, V. Rogers, P.W.G. Smith and A.R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry, 4th ed.*, Longman, New York, 1980, p. 881.
10 K.-B. Shiu and C.-J. Chang, *J. Chin. Chem. Soc. (Taipei)*, 34 (1987) 297.
11 For examples, see (a) R.W. Balk, D.J. Stufkens and A. Oskam, *Inorg. Chim. Acta*, 28 (1978) 133; (b) reference 5; (c) M.N. Ackermann, C.R. Barton, C.J. Deodene, E.M. Specht, S.C. Keill, W.E. Schreiber and H. Kim, *Inorg. Chem.*, 28 (1989) 397.
12 (a) F.A. Cotton and C.S. Kraihanzel, *J. Am. Chem. Soc.*, 84 (1962) 4432; (b) C.S. Kraihanzel and F.A. Cotton, *Inorg. Chem.*, 2 (1963) 533.
13 M.H. Chisholm, J.A. Connor, J.C. Huffman, E.M. Kober and C. Overton, *Inorg. Chem.*, 23 (1984) 2298.
14 L.A. Oro, M. Esteban, R.M. Claramunt, J. Elguero, C. Foces-Foces and F.H. Cano, *J. Organomet. Chem.*, 276 (1984) 79.
15 J.S. Butler and J.F. Harrod (Ed.), *Inorganic Chemistry*, Benjamin and Cummings, New York, 1989, p. 48.