Organotransition-Metal Complexes of Multidentate Ligands. 7. Polypyrazolylamine Complexes of Chromium(II), Molybdenum(II), and Tungsten(II). Stereochemically Nonrigid and Rigid Pseudooctahedral Molecules[1]

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Except for (bdmpam)Cr(CO)$_3$, all other (N-N-N)M(CO)$_3$ compounds readily reacted with allyl bromide in the presence of excess KPF$_6$ to give [(N-N-N)M(CO)$_2(\pi$-C$_3$H$_5$)]PF$_6$ (N-N-N = bpam, M = Cr (1), Mo (2), W (3); N-N-N = bdmpam, M = Mo (4), W (5)) where bpam is *N,N*-bis(pyrazol-1-ylmethyl)aminomethane and bdmpam is *N,N*-bis[(3,5-dimethylpyrazol-1-yl)methyl]aminomethane. The symmetric and/or unsymmetric orientations of the π-allyl group with respect to the N-N-N tridentate are found in 1–5; 1 has the symmetric structure and 4 and 5 have the unsymmetric structure, while both types are present for 2 and 3 in solution. At room temperature, 1, 4, and 5 are rigid whereas 2 and 3 show dynamic behavior. The structural characterization of 2 and the variable-temperature NMR studies establish 2 and 3 as the first stereochemically nonrigid examples among all the π-allyl dicarbonyl complexes containing a neutral chelate.

Introduction

We have recently described the synthesis of (N-N-N)-M(CO)$_3$ compounds (N-N-N = bpam, bdmpam; M = Cr, Mo, W),[1a] the first well-characterized polypyrazolylamine derivatives of metal carbonyls, where bpam is *N,N*-bis-(pyrazol-1-ylmethyl)aminomethane and bdmpam is *N,N*-bis[(3,5-dimethylpyrazol-1-yl)methyl]aminomethane (Figure 1). Over the past 20 years, polypyrazolylborate has been shown to have a rich coordination chemistry,[3] hence, the closely related polypyrazolylamine is expected to form a wide variety of complexes which may have interesting chemical properties. Although the polypyrazolylamine ligands are analogous to other nitrogen tridentates such as diethylenetriamine (dien) or bis(2-pyridylmethyl)amine (bpma), it is anticipated that the ligands may cause the resulted complexes to behave differently in solution because of the π acidity[4] of the pyrazolyl group. We report here the synthesis, structure, and solution behavior of [(N-N-N)M(CO)$_2(\pi$-C$_3$H$_5$)]PF$_6$ (N-N-N = bpam, M = Cr (1), Mo (2), W (3); N-N-N = bdmpam, M = Mo (4), W (5)).

Results and Discussion

Synthesis. Except for (bdmpam)Cr(CO)$_3$, all other (N-N-N)M(CO)$_3$ compounds readily reacted with allyl bromide in the presence of excess KPF$_6$ to give [(N-N-

N)M(CO)$_2(\pi$-C$_3$H$_5$)]PF$_6$ (1–5). These compounds were characterized by infrared spectroscopy and microanalysis (Table I) and ^{1}H and ^{13}C NMR spectroscopy (Tables II and III).

Addition of allyl bromide to (bpam)Cr(CO)$_3$ in CH$_3$CN at room temperature or at 50 °C does not result in the formation of the expected [(bdmpam)Cr(CO)$_2(\pi$-C$_3$H$_5$)]Br but at 84 °C gradually affords decomposition products. Thus, the two ligands bpam and bdmpam must influence the reactivity of (N-N-N)Cr(CO)$_3$ differently, and this difference is not observed for either (N-N-N)Mo(CO)$_3$ or (N-N-N)W(CO)$_3$ complexes. Since the weighted average values of the ν(CO) of (N-N-N)M(CO)$_3$ are close to each other,[1a] we believe that the steric effect of the ligands are more important than the electronic effect in the oxidative allylation of (N-N-N)M(CO)$_3$. The methyl groups on the ring 3-position increases the steric bulk of bdmpam relative to bpam, and according to the periodic trend chromium has a smaller size than molybdenum or tungsten in the same oxidation state. Hence, the bdmpam ligand may protect the chromium atom in (bdmpam)Cr(CO)$_3$ very effectively and retard allylation at 50 °C or lower temperature. Since [(bpam)Cr(CO)$_2(\pi$-C$_3$H$_5$)]PF$_6$ is found to be heat-sensitive, it may be possible that [(bdmpam)Cr-(CO)$_2(\pi$-C$_3$H$_5$)]PF$_6$ is formed in boiling CH$_3$CN but decomposes as rapidly as it is formed.

Characterization. Since both bpam and bdmpam ligands are symmetric ligands (Figure 1), the ^{1}H NMR spectral features of the two methylene groups and the syn and the antiprotons of the π-allyl group in 1–5 are very informative about the unsymmetric, I, or symmetric, II, orientation of the allyl group with respect to the N-N-N ligands (Figure 2). At 294 K or above, ^{1}H NMR spectra of 1–3 showed different features from 4 and 5 (Table II). The methylene protons in 4 and 5 gave two AB quartets while those in 1–3 exhibited only an AB quartet. Apparently coincidently, either the anti or the syn protons of the allyl group in 4 and 5 displayed two doublets whereas those in 1–3 showed a doublet. If 1–5 are rigid in solution, these patterns indicate that 1–3 probably adopt the symmetric structure, II, while 4–5 probably adopt the unsymmetric structure, I. Whether the cations are rigid

(1) (a) Part 1: Shiu, K.-B.; Vong, W.-J.; *J. Chin. Chem. Soc. (Taipei)* 1987, *34*, 195. (b) Part 2: Shiu, K.-B.; Chang, C.-J. *Ibid.* 1987, *34*, 297. (c) Part 3: Shiu, K.-B.; Liou, K.-S. *Ibid.* 1988, *35*, 187. (d) Part 4: Shiu, K.-B.; Lee, L.-Y. *J. Organomet. Chem.* 1988, *348*, 357. (e) Part 5: Shiu, K.-B.; Chang, C.-J.; Wang, Y.; Cheng, M.-C. *J. Chin. Chem. Soc. (Taipei)* 1989, *36*, 25. (f) Part 6: Shiu, K.-B.; Lee, L.-Y. *Ibid.* 1989, *36*, 31. (g) Part 8: Shiu, K.-B.; Liou, K.-S.; Wang, S.-L.; Cheng, C. P.; Wu, F.-J. *J. Organomet. Chem.* 1989, *359*, C1.

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(3) (a) Trofimenko, S. *Acc. Chem. Res.* 1971, *4*, 17. (b) Trofimenko, S. *Chem. Rev.* 1972, *72*, 497. (c) Trofimenko, S. *Adv. Chem.* 1976, *150*, 289. (d) Shaver, A. *J. Organomet. Chem. Libr.* 1977, *3*, 157. (e) Trofimenko, S. *Prog. Inorg. Chem.* 1986, *34*, 115.

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(5) Breakell, K. R.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* 1979, *57*, 139.

Table I. Infrared and Microanalytical Data

complex	yield, %	$\nu(CO)$,[a] cm^{-1}	$\nu(CO)_{av}$, cm^{-1}	anal. found (calcd) C	H	N
[(bpam)Cr(CO)$_2$(π-C$_3$H$_5$)]PF$_6$ (1)	81	1953, 1866	1910	34.47 (34.65)	3.75 (3.74)	14.25 (14.43)
[(bpam)Mo(CO)$_2$(π-C$_3$H$_5$)]PF$_6$ (2)	80	1976, 1879	1928	31.67 (31.77)	3.40 (3.43)	13.19 (13.23)
[(bpam)W(CO)$_2$(π-C$_3$H$_5$)]PF$_6$ (3)	96	1968, 1875	1922	26.90 (27.24)	2.91 (2.94)	11.07 (11.35)
[(bdmpam)Mo(CO)$_2$(π-C$_3$H$_5$)]PF$_6$ (4)	98	1966, 1874	1920	36.56 (36.94)	4.52 (4.48)	11.62 (11.96)
[(bdmpam)W(CO)$_2$(π-C$_3$H$_5$)]PF$_6$ (5)	89	1956, 1854	1905	31.75 (32.11)	3.87 (3.86)	10.26 (10.40)

[a] In CH$_2$Cl$_2$.

Table II. ¹H NMR Data (δ)

complex	condns	allyl[a] H$_a$	H$_s$	H$_c$	tridentate ligand[b] N–CH$_2$–N	N–CH$_\beta$	R$_3$/R$_5$	R$_4$
1	100 MHz, CD$_3$CN, 296 K	1.42 d (9.8)	4.24 d (6.0)	4.83 m	4.96 d (11.8) 5.17 d (11.8)	4.22 s	7.43 d (2.0) 7.60 d (2.0)	6.16 t
1	400 MHz, (CD$_3$)$_2$CO, 294 or 243 K	1.51 d (9.6)	4.37 d (6.3)	5.09 m	5.45 d (11.8) 5.52 d (11.8)	4.41 s	7.69 br[c] 7.86 br	6.27 br
2	100 MHz, (CD$_3$)$_2$CO, 296 K	1.58 d (9.8)	3.61 d (6.6)	4.27 m	5.30 d (12.1) 5.52 d (12.1)	3.53 s	7.79 d (2.5) 7.87 d (1.8)	6.32 t
2	400 MHz, (CD$_3$)$_2$CO, 318 K	1.57 br	3.62 d (6.4)	4.23 m	5.23 d (12.1) 5.42 d (12.1)	3.49 s	7.73 d (2.0) 7.83 br	6.30 br
		(1.55)[d]	(3.58)	(4.27)	(5.26, 5.48)	(3.50)	(7.72), 7.89)	(6.31)
2(I)	400 MHz, (CD$_3$)$_2$CO, 238 K	1.23 d (9.6) 1.86 d (9.2)	3.63 d (6.2) 3.60 d (5.5)	4.31 m	5.09 d (12.3) 5.32 d (12.3) 5.23 d (11.8) 5.43 d (11.8)	3.09 s	7.67 br 7.83 br 7.84 br 8.17 br	6.44 br 6.24 br
2(II)	400 MHz, (CD$_3$)$_2$CO, 238 K	1.55 d (9.2)	3.55 d (6.2)	4.22 m	5.46 d (12.0) 5.62 d (12.0)	4.12 s	7.67 br 7.75 br	6.26 br
3	400 MHz, (CD$_3$)$_2$CO, 300 K	1.73 br	3.36 d (4.9)	3.53 m	5.70 d (10.6) 5.37 d (10.6)	3.70 s	7.90 br	6.36 t
3(I)	400 MHz, (CD$_3$)$_2$CO, 230 K	1.41 d (9.0) 1.97 d (8.4)	3.31 br 3.32 br	3.62 br	5.81 d (11.7) 5.68 d (11.9) 5.44 d (11.7) 5.31 d (11.9)	4.38 s	8.33 br 8.11 br 8.02 br 7.94 br	6.37 br 6.56 br
3(II)	400 MHz, (CD$_3$)$_2$CO, 230 K	1.71 d (8.4)	3.51 br	3.58 br	5.98 d (12.0) 5.61 d (12.0)	4.38 s	8.02 br 7.82 br	6.42 br
4	300 MHz, (CD$_3$)$_2$CO, 296 or 233 K	1.15 d (9.8) 2.00 d (9.8)	3.59 d (6.1) 3.61 d (6.1)	4.25 m	4.85 d (11.9) 4.90 d (12.7) 5.25 d (12.7) 5.31 d (11.9)	3.02 s	2.20 s 2.28 s 2.43 s 2.70 s	5.90 s 6.09 s
5	400 MHz, (CD$_3$)$_2$CO, 294 or 233 K	1.32 d (10.1) 2.13 d (10.1)	3.26 d (5.9) 3.40 d (5.9)	3.52 m	4.91 d (11.9) 5.00 d (12.1) 5.46 d (12.1) 5.55 d (11.9)	3.15 s	2.27 s 2.32 s 2.44 s 2.74 s	5.96 s 6.14 s

[a] H$_a$ = anti-protons; H$_s$ = syn-protons; H$_c$ = central proton. [b] R$_3$ = R$_4$ = R$_5$ = H in 1–3; R$_3$ = R$_5$ = CH$_3$, R$_4$ = H in 4 and 5. [c] An unresolved doublet, triplet, or multiplet. [d] Calculated values (see text).
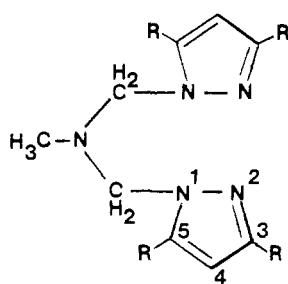

Figure 1. Structural formula of bpam (R = H) and bdmpam (R = CH$_3$).

or not, the solution infrared measurements in CH$_2$Cl$_2$ (Table I) confirm the presence of *cis*-dicarbonyl groups.

In view of the unsymmetric structure[5] of (π-2-methyl-allyl)[hydroxymethylbis(3,5-dimethylpyrazol-1-yl)-gallato]dicarbonylmolybdenum, it seems unusual that **1–3** should take a symmetric structure. Therefore, **2** was structurally characterized. Two different molecules, A and B, were present in each asymmetric unit of the single crystal of **2**. Each cation can be described as pseudooc-tahedral with the assumption that the allyl moiety occupies one coordination site. Since the allyl group takes a position trans to one of the pyrazolyl ring nitrogen atoms, each
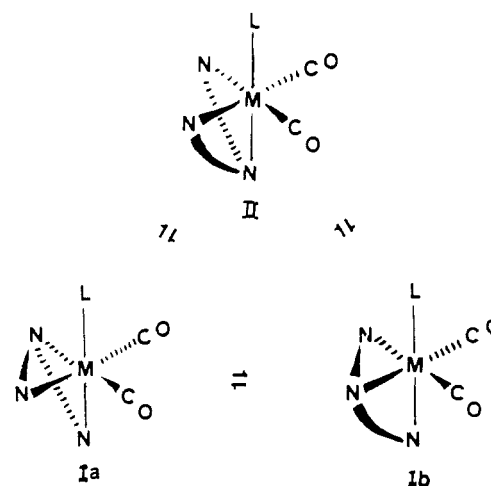

Figure 2. The nondissociative trigonal twist rearrangement between a pair of the unsymmetric enantiomers (Ia and Ib) and the symmetric isomer (II) proposed for the cations [(N-N-N)M-(CO)$_2$L]$^+$ (L = π-allyl) in solution.

cation has the unsymmetric geometry, I. Under constraints of the space group $P\bar{1}$, there are two cation pairs of un-symmetric enantiomers and four anions, PF$_6^-$, in each unit

<div align="center">Table III. $^{13}C\{^1H\}$ NMR Data[a]</div>

complex	condns	CO	allyl		tridentate ligand					
			$C_{terminal}$	$C_{central}$	N-CH$_3$	N-CH$_2$-N	C$_3$	C$_4$	C$_5$	C-CH$_3$
1	100.6 MHz, (CD$_3$)$_2$CO, 294 or 243 K	233.1[†]	69.1[†]	77.3	51.4	74.2[†]	143.5[†]	109.7[†]	133.1[†]	
2	100.6 MHz, CD$_2$Cl$_2$, 294 K	224.8[†]	57.6[†]	71.0	48.3	73.4[†]	144.2[†]	109.9[†]	133.2[†]	
2	100.6 MHz, (CD$_3$)$_2$CO, 318 K	226.0[†]	58.2[†]	72.0	48.6	74.5[†]	144.9[†]	109.2[†]	133.6[†]	
		(226.5)[b]	(58.2)	(71.5)	(48.8)	(74.3)	(14.8)	(109.1)	(133.6)	
2(I)	100.6 MHz, (CD$_3$)$_2$CO, 238 K	225.7	54.4	71.7	46.1	74.2	145.2	108.7	133.8	
		227.8	62.8			75.0	145.9	109.6	133.7	
2(II)	100.6 MHz, (CD$_3$)$_2$CO, 238 K	226.1[†]	57.7[†]	71.1	52.9	73.8[†]	143.7[†]	109.0[†]	133.3[†]	
3	100.6 MHz, (CD$_3$)$_2$CO, 320 K	*	*	63.1	*	74.9[†]	145.2[†]	108.2[†]	133.7[†]	
3(I)	100.6 MHz, (CD$_3$)$_2$CO, 230 K	216.8	45.3	61.5	45.7	73.8	144.9	108.5	132.9	
		218.2	53.2			74.4	145.7	109.3	133.0	
3(II)	100.6 MHz, (CD$_3$)$_2$CO, 230 K	218.8[†]	48.0[†]	61.1	53.2	72.8[†]	142.6[†]	108.6[†]	133.6[†]	
4	75.5 MHz, (CD$_3$)$_2$CO, 296 or 233 K	225.6	52.1	71.7	45.1	72.6	153.8	108.6	143.6	11.1[†]
		227.8	66.5			74.7	155.9	109.8	144.1	15.2, 15.8

[a] The dagger (†) represents a signal produced by two carbon atoms; any other chemical shift (in ppm) represents a signal produced by one carbon atom. The asterisk (*) represents the signal not observed. [b] Calculated values (see text).
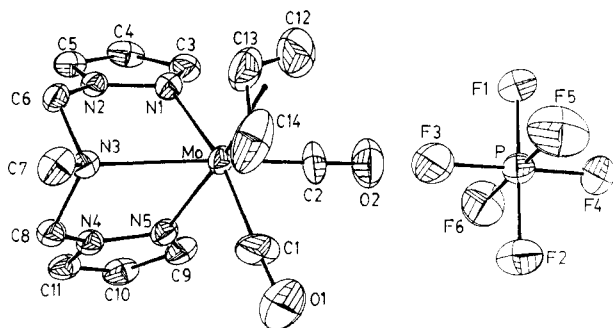

Figure 3. ORTEP drawing of [(bpam)Mo(CO)$_2$(π-C$_3$H$_5$)]PF$_6$ showing the atom numbering scheme. The thermal ellipsoids are drawn at 50% probability level.

cell. From the close similarity in bond lengths and the small differences in bond angles (Table IV), we believe that the existence of two molecules in the asymmetric unit probably results from crystal packing. In solution there is only one pair of enantiomers for 2. Figure 3 shows the ORTEP drawing of A.

How can we explain the ^{1}H NMR spectral features observed for 2? Can the features be ascribed to fluxional behaviors of molecules in solution so that a nondissociative trigonal twist rearrangement occurs between the pair of enantiomers in the same way as that described,[6] i.e., Ia $\rightleftharpoons$ Ib (Figure 2), for [(dien)Mo(CO)$_2$(π-C$_3$H$_5$)]PF$_6$ or [(bpma)Mo(CO)$_2$(π-C$_3$H$_5$)]PF$_6$ by Brisdon and his co-workers? In order to better compare their and our systems, we studied the variable-temprature behavior of 2 in solution by using a Bruker WP-100 spectrometer. At 243 K or below, we observed two apparently overlapping AB quartets that we assign to the methylene protons, a feature they described in their paper. However, there are always three clear doublets in an integration ratio close to be 3:4:3 that can be assigned to the antiprotons of the allyl group. This observation led us to believe that the mechanism of the fluxional process in our system may be different from that they described. We then reinvestigated the variable-temperature behavior of 2 by using a Bruker AM-400 spectrometer.[7] In order to make unambiguous assign-

(6) Brisdon, B. J.; Cartwright, M.; Hodson, A. G. *J. Oganomet. Chem.* **1984**, *277*, 85.

(7) The coupling between protons in the pyrazolyl rings were not observed in the ^{1}H NMR spectra measured by the 400-MHz spectrometer. It should be contrasted with the clear splitting patterns ($J \approx 2$ Hz) for spectra observed with a 100-MHz spectrometer (Table II). The difference is due to the faster T_2 relaxation rate at 400 MHz compared with that at 100 MHz because of the magnitude of $\omega_o\tau_c{}^8$ is different at the two frequencies.

Table IV. Selected Bond Lengths (Å) and Angles (deg) in 2

<div align="center">a. Bond Lengths</div>

bond	2A	2B	$|\Delta|^a$
Mo-N(1)	2.387 (4)	2.263 (4)	0.124 (8)
Mo-N(3)	2.587 (4)	2.577 (4)	0.010 (8)
Mo-N(5)	2.190 (4)	2.195 (4)	0.005 (8)
Mo-C(1)	2.079 (6)	1.988 (6)	0.08 (1)
Mo-C(2)	2.066 (6)	2.090 (6)	0.02 (1)
Mo-C(12)	2.336 (6)	2.430 (9)	0.09 (2)
Mo-C(13)	2.226 (5)	2.198 (7)	0.03 (1)
Mo-C(14)	2.343 (5)	2.364 (7)	0.02 (1)

<div align="center">b. Bond Angles</div>

bond angle	2A	2B	$|\Delta|^a$
N(1)-Mo-N(3)	67.8 (1)	79.5 (1)	11.7 (2)
N(1)-Mo-N(5)	77.2 (2)	77.7 (2)	0.5 (4)
N(1)-Mo-C(1)	168.3 (2)	164.9 (2)	3.4 (4)
N(1)—Mo-C(2)	108.3 (2)	92.5 (2)	15.8 (4)
N(1)-Mo-Ct[b]	96.2 (1)	101.5 (1)	5.3 (2)
N(3)-Mo-N(5)	73.9 (1)	74.0 (1)	0.1 (2)
N(3)-Mo-C(1)	106.3 (2)	97.6 (3)	8.7 (5)
N(3)-Mo-C(2)	164.2 (2)	166.5 (2)	2.3 (4)
N(3)-Mo-Ct	102.52 (9)	99.35 (9)	3.2 (2)
N(5)-Mo-C(1)	91.6 (2)	87.3 (2)	4.3 (4)
N(5)-Mo-C(2)	90.3 (2)	93.8 (2)	3.5 (4)
N(5)-Mo-Ct	173.2 (1)	173.3 (1)	0.1 (2)
C(1)-Mo-C(2)	74.6 (3)	87.3 (3)	12.7 (6)

[a] The absolute value of difference between the corresponding bond lengths or angles in 2A and 2B. [b] Ct is defined as the midpoint of C(12), C(13), and C(14).

ments in ^{1}H and $^{13}C\{^1H\}$ NMR spectra of 2 (Figures 4 and 5), the 2-D NMR spectra were also recorded.

The limiting low-temperature spectra shown in Figure 4 can be obtained in a temperature range below 238 K. It is evident that there are more signals than expected. In the homonuclear ^{1}H–^{1}H COSY spectrum shown in Figure 6, the two anti proton signals of equal intensity at 1.23 (d, $J = 9.6$ Hz) and 1.86 ppm (d, $J = 9.2$ Hz) correlate with the ^{1}H signal at 4.31 ppm (t) whereas the other anti proton signal at 1.55 ppm (d, $J = 9.2$ Hz) correlates with a signal at 4.22 ppm (t). Weak correlation between the anti proton signals with signals around 3.6 ppm (the syn proton signals) can also be observed. Furthermore, the three sets of AB quartets with an intensity ratio of 3:3:4 around 5.4 ppm can be assigned to the methylene protons. This feature apparently echos the three sets of doublets in a ration of 3:4:3 observed for the anti protons of the allyl group.

(8) Becker, E. D. *High Resolution NMR*; Academic: New York, 1980; Chapter 8.
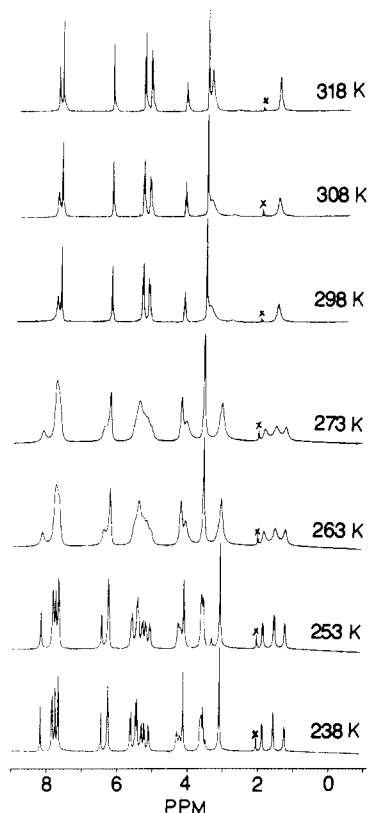
Figure 4. The variable-temperature ^1H NMR spectra of [(bpam)Mo(CO)$_2$(π-C$_3$H$_5$)]PF$_6$ in acetone-d_6. The resonance marked (X) is due to the solvent.
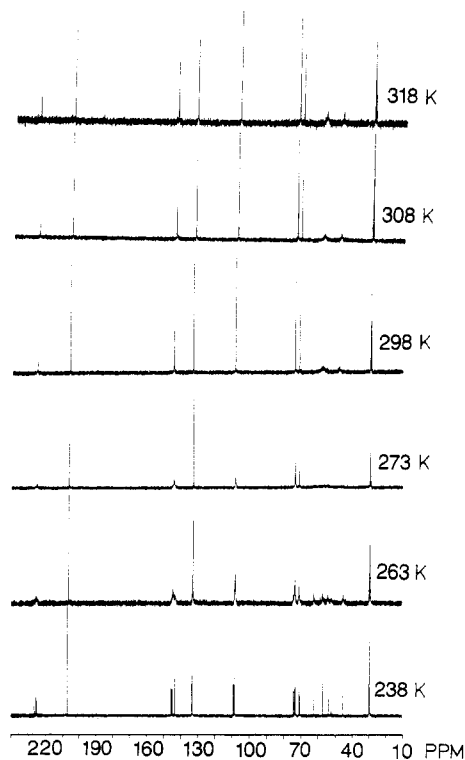
Figure 5. The variable-temperature $^{13}C\{^1H\}$ NMR spectra of [(bpam)Mo(CO)$_2$(π-C$_3$H$_5$)]PF$_6$ in acetone-d_6.

We propose that two different isomers for **2** exist, unsymmetric (I) and symmetric (II) in a relative ratio of 3:2.[9]

Figure 6. The homonuclear ^1H–^1H COSY of [(bpam)Mo-(CO)$_2$(π-C$_3$H$_5$)]PF$_6$ in acetone-d_6. The resonance marked (X) is due to the solvent.

The methyl signal at 3.09 ppm can be assigned to isomer I (anti protons, H$_a$, at 1.23 and 1.86 ppm and syn protons, H$_s$, at 3.63 and 3.60 ppm), while that at 4.12 ppm can be assigned to isomer II (H$_a$ at 1.55 ppm and H$_s$ at 3.55 ppm). The two AB quartets (quartet 1, δ = 5.09, 5.32 ppm (J = 12.3 Hz); quartet 2, δ = 5.23, 5.43 ppm (J = 11.8 Hz)) can be assigned to isomer I and the remaining quartet (δ = 5.46, 5.62 ppm (J = 12.0 Hz)) to isomer II. The signals around 6.2 ppm are attributed to protons at the ring 4-position (isomer I, 6.24 and 6.44 ppm; isomer II, 6.26 ppm). The task of assigning the signals for the corresponding protons at the ring 3- and 5-positions has been shown to be difficult[10] for polypyrazolylborate–metal complexes, and we had similar problems here. We do know on the basis of ^1H–^1H COSY spectra is that the group of signals at 7.67, 7.83, 7.84, and 8.17 ppm is assigned to isomer I and the group of signals at 7.67 and 7.75 ppm is assigned to isomer II. However, since there are many reports[11] of $^{13}C\{^1H\}$ NMR spectra for the molybdenum carbonyl complexes containing the pyrazole-derived ligands, it is now generally accepted that the ^{13}C signals in the range of 130–137 ppm can be assigned to the carbons at ring 5-position and the signals in the range of 140–147 ppm can be assigned to the carbons at the ring 3-position. Thus, through a heteronuclear ^{13}C–^1H COSY spectrum, we can assign the ^1H NMR signals corresponding to protons at the ring 5-position (isomer I, 7.67 and 7.84 ppm; isomer II, 7.75 ppm) and protons at the ring 3-position (isomer I, 7.83 and 8.17

(9) It is not clear at present stage why isomer I vs isomer II is 3:2. Currently, we are pursuing the simulation of the proton NMR spectra to understand the dynamic process. The results will be reported later.
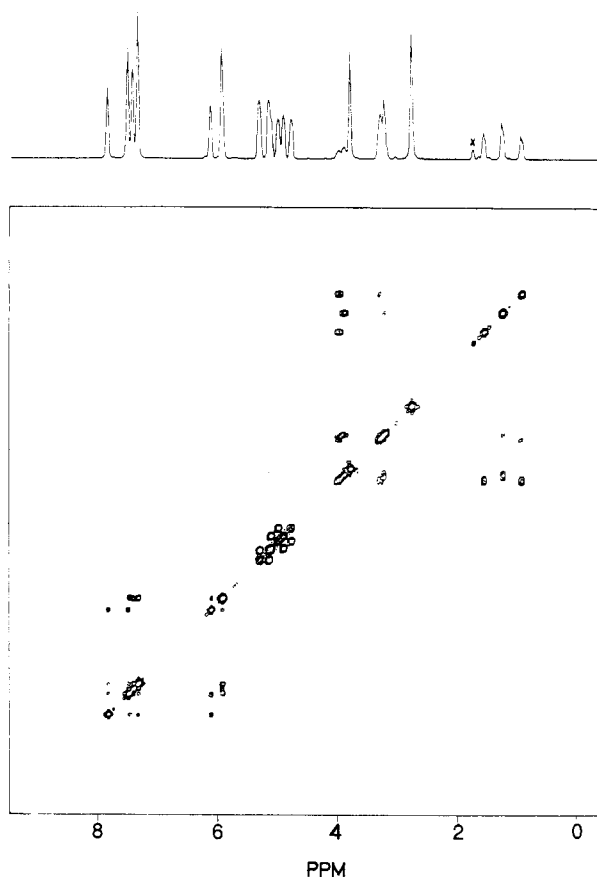
(10) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170.
(11) For examples, see: (a) Curtis, M. D.; Shiu, K.-B. *Inorg. Chem.* **1985**, *24*, 1213. (b) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 5154; (c) Curtis, M. D.; Shiu, K.-B.; Butler, W. M. *Ibid.* **1986**, *108*, 1550.

Table V. The Connected $^{13}C\{^1H\}$ and ^1H NMR Spectral Data (ppm) for 2 at 238 K

isomer 2(I)		isomer 2(II)	
$^{13}C\{^1H\}$	^1H	$^{13}C\{^1H\}$	^1H
54.4	1.23, 3.63	57.7	1.55, 3.55
62.8	1.86, 3.60	71.1	4.22
71.7	4.31	52.9	4.12
46.1	3.09	73.8	5.46, 5.62
74.2	5.09, 5.32	109.0	6.26
75.0	5.23, 5.43	133.3	7.75
108.7	6.24	143.7	7.67
109.6	6.44		
133.7	7.84		
133.8	7.67		
145.2	7.83		
145.9	8.17		

ppm; isomer II, 7.67 ppm). The assignments in the ^1H NMR spectra and the connection between $^{13}C\{^1H\}$ and ^1H NMR data are shown in Tables II and V, respectively.

We also carried out the variable-temperature NMR studies for 1 and 3. Complex 3 did show similar features in which both I and II are present in solution. However, ^1H and $^{13}C\{^1H\}$ NMR spectra of 1 at either room temperature or down to 243 K are similar to each other, indicating that only symmetrical isomer is present. Since the ^1H NMR spectra of 4 or 5 measured at room temperature and 233 K are identical within the experimental errors, complexes 4 and 5 in the unsymmetric structure (I) and complex 1 in the symmetric structure (II) are rigid in solution at room temperature on the NMR time scale.

Why is only one specific structure present for 1, 4, and 5 whereas two structures exist for 2 and 3? We believe that consideration of steric and electronic factors of the central metal atom, M, and the coordinate ligands in 1-5 may answer the question. Under the circumstances of the negligible nonbonded interactions among all the ligands and the similar M-N distances to those reported,[12,13] the strongest π-acid ligand, CO, would prefer to adopt a position trans to the strongest σ-donor ligand, the central, saturated, nitrogen atom ($N_{sat.}$) of the N-N-N ligand, rather than a position trans to one of the remaining unsaturated nitrogen atoms ($N_{unsat.}$) of the ligand, and the unsymmetric structure is more favorable than the symmetric one. In 2, the Mo-N(3) distances of 2.577 and 2.587 Å are far outside the range for a Mo(II)-$N_{sat.}$ distance[12] of 2.240-2.273 Å, indicating that the M-$N_{sat.}$ bond in 2 (and probably in 3) is weaker than that expected while the Mo-N(1) and Mo-N(5) distances of 2.387, 2.263, 2.190, and 2.195 Å are close to the range for a Mo(II)-$N_{unsat.}$ distance[13] of 2.14-2.27 Å showing that the M-$N_{unsat.}$ bonds in 2 (and probably in 3) are in similar strength to those anticipated. Thus, the fact explains why the two structures are present in 2 and 3. Although the average ν(CO) values of 2-5 (Table I) reflect that the bdmpam ligand is a slightly better electron-donating group, the bulkier bdmpam ligand would dislike the symmetric form due to a larger steric repulsion in this form between the allyl group and the two 3,5-dimethylpyrazolyl moieties of the ligand compared with that in the unsymmetric form. Hence, only the unsymmetric form is observed for 4 and 5. Obviously, the smaller metal atom in 1 relative to that in 2 or 3 would lead to the shorter M-N distances in 1 compared with those in 2 or 3. It is thus probably true that in 1 the Cr-$N_{unsat.}$ bonds are much stronger than the Cr-$N_{sat.}$ bond and the steric repulsions

among the ligands are still small. Therefore, two carbonyl adopt the positions trans to the $N_{unsat.}$ atoms of the N-N-N ligand, and the symmetric structure is found for 1.

Mechanism of Interconversion. From the solid-state structure of 2 and the variable-temperature NMR spectra of 2 and 3, we believe that the complexes can be described as stereochemically nonrigid[14] and a nondissociative trigonal twist mechanism containing one pair of unsymmetric enantiomers (Ia and Ib) and the symmetric isomer (II) can account for the solution behavior of 2 and 3, i.e., Ia $\rightleftharpoons$ II $\rightleftharpoons$ Ib (Figure 2). Interconversion of the three configurations is very fast, since the limiting high-temperature spectra of 2 and 3 can be readily observed at temperatures above 294 K (see Figures 4 and 5). For 2, the observed chemical shifts collected in Tables II and III can be calculated on the basis of the chemical shifts of the observed signals at 238 K with the weighting factor of 3/2 for I/II. There is an good agreement between the calculated and observed $\delta(^{13}C)$ or $\delta(^1H)$. The agreement supports the proposal that both I and II are present[9] in solution, at least within the experimental range of 238-318 K for 2, and the suggested mechanism. Since the NMR spectra of 3 showed similar features as those of 2, the mechanism of interconversion can also be applied for 3. Thus, 2 and 3 represent the first stereochemically nonrigid examples among all the pseudooctahedral π-allyl dicarbonyl complexes containing a neutral chelate.[6,15]

Summary

The two isomeric structures depicted in Figure 2 are possible for cations of 1-5; the N-N-N ligand is either unsymmetrically or symmetrically bound with respect to the allyl group. By virtue of NMR results, cations 4 and 5 have the unsymmetric structure I while 1 has the symmetric structure II. Cations of three complexes, 1, 4 and 5, are rigid in solution at room temperature. In contrast to the fluxional behavior between a pair of unsymmetric enantiomers (Ia $\rightleftharpoons$ Ib) observed for the cations [(dien)-Mo(CO)$_2$(π-C$_3$H$_5$)]$^+$ and [(bpma)Mo(CO)$_2$(π-C$_3$H$_5$)]$^+$,[6] the solid-state structure of 2 and the variable-temperature NMR studies of 2 and 3 establish that both the unsymmetric and symmetric structures are present in solution for which a stereochemically nonrigid process (Ia $\rightleftharpoons$ II $\rightleftharpoons$ Ib) can be assumed (Figure 2). Among all the metal π-allyl dicarbonyl complexes including a neutral chelate,[6,15] 2 and 3 represent the first nonrigid examples.

Experimental Section

All operations were carried out under N_2 by standard Schlenk and vacuum-line techniques. Organic solvents were dried by standard procedures and distilled under N_2 before use. IR spectra, calibrated with polystyrene, were recorded on a Hitachi 260-30 model instrument. NMR spectra were obtained on a Bruker WP-100 (^1H, 100; ^{13}C, 25.2 MHz), AM-300 (^1H, 300; ^{13}C, 75.5 MHz), or AM-400 (^1H, 400; ^{13}C, 100.6 MHz) FT NMR spectrometer using internal deuterium lock solvents and tetramethylsilane standard. Elemental analysis results were obtained by the staff of the Microanalytical Service of the Department of Chemistry, National Cheng Kung University. (N-N-N)M(CO)$_3$ (N-N-N = bpam, bdmpam; M = Cr, Mo, W) were prepared by literature methods[1a].

Preparation of [(bpam)Cr(CO)$_2$(π-C$_3$H$_5$)]PF$_6$ (1). A stirred solution of (bpam)Cr(CO)$_3$ (0.170 g, 0.52 mmol) in CH$_3$CN (30 mL) was treated with 1 mL of allyl bromide. The solution soon changed color from orange-yellow to red and gas evolved. After 15 min, KPF$_6$ (1.400 g, 7.61 mmol) was added to the solution.

(12) Chaudhuri, P.; Wieghardt, K.; Tsai, Y.-H.; Kruger, C. *Inorg. Chem.* **1984**, *23*, 427.

(13) Lincoln, S.; Song, S. L.; Koch, S. A.; Sato, M.; Enemark, J. H. *Inorg. Chem.* **1985**, *24*, 1355 and references cited therein.

(14) Muetterties, E. L. *Acc. Chem. Soc.* **1970**, *3*, 266.

(15) Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865.

Table VI. Crystallographic Data for [(bpam)Mo(CO)₂(π-C₃H₅)]PF₆

formula	$C_{14}H_{18}F_6MoN_5O_2P$
mol wt	529.05
space group	$P\bar{1}$
a, Å	9.963 (2)
b, Å	14.997 (2)
c, Å	16.638 (3)
α, deg	112.65 (1)
β, deg	78.14 (1)
γ, deg	103.08 (2)
V, Å³	2215.22
Z	4
d_{calcd}, g cm⁻³	1.587
temp, K	300
radiatn	Mo Kα (λ = 0.710 69 Å)
cryst dimens, nm	0.2 × 0.3 × 0.5
μ, cm⁻¹	7.1
2θ range, deg	50
scan speed, deg min⁻¹	1.25–10
reflecns measd	$\pm h, +k, \pm l$
reflecns collected	7009
reflecns with $I > 3\sigma(I)$	5203
no. of variables	523

Stirring was continued for 10 more minutees, and the solvent was then removed in vacuo leaving a solid residue. CH₂Cl₂ (10 mL) was added, and the resulted suspension was filtered through a medium frit. The solvent was removed from the filtrate under vacuum giving orange-red solid (0.205 g, 81%). The compound is *heat-sensitive* and gradually decomposed in boiling CH₃CN.

Attempted Formation of (bdmpam)Cr(CO)₂(π-C₃H₅)PF₆. A stirred solution of (bdmpam)Cr(CO)₃ (0.096 g, 0.25 mmol) in 50 mL of CH₃CN was added dropwise with allyl bromide (0.031 g, 0.25 mmol). After 30 min, a solution IR spectrum did not show any new carbonyl stretching bands. The stirring was continued for a total of 2 h in a water bath at 50 °C. Since no new bands were observed again, the solution was heated at 82 °C. The solution changed color gradually from orange-yellow to green. An IR spectrum of the green solution displayed no carbonyl stretching bands in a range of 2200–1600 cm⁻¹.

General Procedure for the Preparation of (N-N-N)M′-(CO)₂(π-C₃H₅)PF₆ (M′ = Mo, W). To a solution of (N-N-N)-M′(CO)₃ (5.0 mmol) in 30 mL of CH₃CN was added 1 mL of allyl bromide. The mixture was heated at 82 °C for 30 min before addition of 1.60 g of KPF₆ (8.70 mmol). The resulted suspension was then stirred for 1 h and filtered. The solvent was stripped off from the filtrate leaving an orange-yellow residue. Recrystallization from CH₂Cl₂/hexane gave pure products. Yields are 80, 96, 98, and 89% for 2, 3, 4, and 5, respectively (Table I).

X-ray Structure Analysis of (bpam)Mo(CO)₂(π-C₃H₅)PF₆. Collection and Reduction of X-ray Data. An orange crystal with approximate dimensions 0.2 × 0.3 × 0.5 mm, grown from CH₂Cl₂/hexane at room temperature, was mounted on the end of a glass fiber. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer. Programs of the structural determination package developed by the National Research Council of Canada[16] were used for solution and structural refinement. All calculations were performed on a PDP 11/23 computing system. A set of 25 centered reflections collected (23.12 < 2θ < 30.58°) and refined by least-square calculations indicated a triclinic cell.

Data were collected under the conditions specified in Table VI. Three reflections chosen as intensity standards were monitored every 3 h and indicated less than 2% decay. Three orientation standards were checked after every 300 reflections, and the crystal was recentered if the scattering vectors differed by more than 0.2. Data reduction was then performed, and empirical absorption corrections (μ = 7.1 cm⁻¹; calculated transmission range 0.96–1.00) using psi scans were also made before registration of the data. A total of 5203 reflections with $I > 3\sigma(I)$ were considered as observed and used for structure resolution.

Structure Solution and Refinement. Application of the heavy-atom method showed two molecules per asymmetric unit (four molecules per unit cell). Two molybdenum atoms were located in the three-dimensional Patterson function. Subsequent Fourier and difference Fourier calculations revealed the remaining non-hydrogen atoms. Least-squares refinements of 58 non-hydrogen atoms with anisotropic factors using the observed reflections resulted in unweighted (R) and weighted residuals (R_w) of 0.039 and 0.041, respectively.[17] Goodness of fit (GOF)[18] is 3.127. Hydrogen atoms with the isotropic temperature parameters set at 8.0 e/Å³ were positioned from a difference Fourier. The subsequent Fourier is featureless with the largest peak having an intensity of 0.74 e/Å³.

Supplementary Material Available: Tables of fractional atomic coordinates, complete bond lengths and angles, anisotropic thermal parameters, and hydrogen parameters for A and B of 2 (7 pages); listings of structure factors (F_o vs F_c) for 2 (47 pages). Ordering information is given on any current masthead page.

(16) (a) Gabe, E. J.; Lee, F. L. *Acta Crystallogr., Sect. A* 1981, *A37*, S330. (b) Enraf-Nonius, *Structure Determination Package*, Enraf-Nonius, Deft, The Netherlands, 1979.

(17) $R = \sum ||F_o| - |F_c||/\sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = (1/\sigma^2)|F_o|$.

(18) GOF = $[\sum(w|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO = number of observed reflections and NV = number of variables.