Complexes of 1,8-Naphthyridines. VI. Mixed Ligand Complexes of Molybdenum Hexacarbonyl

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Complexes of the type $Mo(CO)_3(N-N)L$ and $Mo(CO)_2$-$(N-N)L_2$ where N-N is 2,7-dimethyl-1,8-naphthyridine, 2,7-dmnapy, or 2,9-dimethyl-1,10-phenanthroline, 2,9-dmphen, and L is a monodentate Lewis base have been prepared and characterized by infrared and proton magnetic resonance spectroscopy. The positions observed for the CO stretching modes of these complexes as well as the separation of the A'_2 and A'' modes of the tricarbonyl compounds suggests that the π-accepting ability of 2,7-dmnapy may be slightly greater than 2,2'-bipyridine, 1,10-phenanthroline or 2,9-dmphen. The ease of displacement N-N by Lewis bases is dependent on the concentration and steric nature of the phosphorus donor and follows the order 2,7-dmnapy > bipy > phen ~ 2,9-dmphen. The unexpected shielding of N-N and L protons in the pmr spectra is discussed in terms of anisotropy produced by the aromatic systems.

Introduction

In recent years, Group VIb carbonyl complexes which contain at least two different Lewis bases have been intensely studied in an attempt to elucidate the relationship between carbonyl absorptions observed in the infrared spectra and bonding of the bases to the metal.[2-5] Although the geometry about the central metal can be established from the number and relative intensities of these bands,[6,7] whether or not the amount of pi back bonding from the metal to the ligand moiety can be infererd from the positions of these bands has been the subject of extended controversy.[8,9,10] As a result of these investigations one can only conclude that the sigma bonding ability of the Lewis base can no longer be neglected when attempting to account for shifts in the carbonyl stretching frequencies of the complexes.

The preparation of mixed complexes amenable to

study by proton magnetic resonance as well as infrared spectroscopy provide a supplemental means of evaluating π-bonding arguments. In addition, the two nitrogen heterocycles chosen for this study provide the opportunity to compare the bonding properties of four- and five-membered chelate systems.

Experimental Section

Materials. Molybdenum hexacarbonyl was a generous gift from Climax Molybdenum Co. The procedure of Paudler and Kress[11] was used for the preparation of 2,7-dimethyl-1,8-naphthyridine (2,7-dmnapy). 2,9-Dimethyl-1,10-phenanthroline (2,9-dmphen), was purchased from G. Frederick Smith Chemical Co.. 5,5-Dimethyl-2-phenoxy-1,3,2-dioxaphosphorinane (DP-DP), was a generous gift from the Hooker Chemical Co. All other Lewis bases are commercially available (Eastman Chemical) and were used without further purification. All solvents were ACS grade which had been dried and stored over molecular sieves and/or sodium.

Preparations. $Mo(CO)_4(2,7\text{-dmnapy})$ and $Mo(CO)_4$-$(2,9\text{-dmphen})$ were prepared as outlined elsewhere.[12] The complexes $Mo(CO)_3(N-N)L$ where (N-N) is 2,7-dmnapy or 2,9-dmphen and L is one of the Lewis bases given in Table I were prepared by direct reaction of $Mo(CO)_4(N-N)$ and L (1:1) under Helium in 25 ml of refluxing solvent. Reaction times and solvents are listed in Table I. The $Mo(CO)_2(N-N)L_2$ complexes were prepared in a similar manner except that a 1:2 ratio of starting materials was employed. The compounds were isolated by suction filtration and washed on the filter with pentane or anhydrous diethylether. In some cases it was necessary to reduce the volume of the solution by vacuum evaporation to obtain a filterable product. Most compounds were obtained analytically pure in quantitative yields. The impure products (indicated by ^{a} in Table I) were chromatographed on Fisher A-540, 80-200 mesh, alumina. These complexes were loaded onto the column with benzene and eluted with methylene chloride. The methylene chloride fraction was either evaporated to dryness or treated with hexane and evaporated until a

(1) Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minnesota, April 17, 1969, Abstract No. INOR 132.
(2) G. R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, 1, 287 (1967).
(3) R. J. Angelici and J. R. Graham, *Inorg. Chem.*, 6, 988 (1967).
(4) J. Dalton, 1. Paul, J. G. Smith, and F. G. A. Stone, *J. Chem. Soc.*, (A), 1208 (1968).
(5) R. J. Angelici, *Organometal. Chem. Rev.*, 3, 173 (1968).
(6) T. A. Manuel, *Advan. Organomet. Chem.*, 3, 181 (1965).
(7) L. E. Orgel, *Inorg. Chem.*, 1, 25 (1962).
(8) W. D. Horrocks, Jr., and R. C. Taylor, *Inorg. Chem.*, 2, 723 (1963).
(9) R. J. Angelici, *J. Inorg. Nuclear Chem.*, 28, 2627 (1966).
(10) R. J. Angelici and C. M. Ingemanson, *Inorg. Chem.*, 8, 83 (1969).

(11) W. W. Paudler and T. J. Kress, *J. Heterocycl. Chem.*, 4, 284 (1967).
(12) D. G. Hendricker and T. E. Reed, *Inorg. Chem.*, 8, 685 (1969).

Table I. Analytical and Preparative Data

Compound	Preparation		Analyses % Carbon		% Hydrogen		% Nitrogen	
	Solvent	Time	Calcd.	Found	Calcd.	Found	Calcd.	Found
$Mo(CO)_3(2,7\text{-dmnapy})(NC_5H_5)$	Octane	2 hr	51.80	51.78	3.62	3.44	10.07	10.23
$Mo(CO)_3(2,7\text{-dmnapy})(NC_5H_4\text{-}3\text{--}CH_3)$	Xylene	4 hr	52.90	52.73	3.97	3.95	9.74	9.56
$Mo(CO)_3(2,7\text{-dmnapy})(NC_5H_4\text{-}2\text{--}NH_2)$	Octane	3 hr	50.00	50.03	3.73	3.71	12.96	13.06
$Mo(CO)_3(2,7\text{-dmnapy})(NC_5H_4\text{-}3\text{--}NH_2)$	Octane	1 hr	50.00	50.65	3.73	3.81	12.96	13.11
$Mo(CO)_3(2,7\text{-dmnapy})(CH_3CN)$	Heptane	4 hr	47.50	47.41	3.45	3.40	11.08	10.86
$Mo(CO)_3(2,7\text{-dmnapy})(HCON(CH_3)_2)$	Octane	2 hr	46.71	46.37	4.17	4.16	10.21	10.21
$Mo(CO)_3(2,7\text{-dmnapy})(P(OCH_3)_3)$ [a]	Octane	1 hr	41.56	41.70	4.14	4.16	6.06	6.38
$Mo(CO)_3(2,7\text{-dmnapy})(P(OC_2H_5)_3)$	Octane	1 hr	45.24	45.00	5.00	5.10	5.55	5.67
$Mo(CO)_3(2,7\text{-dmnapy})(P(O\text{-}i\text{-}C_3H_7)_3)$	Octane	1 hr	48.35	48.44	5.72	5.75	5.13	5.45
$Mo(CO)_3(2,7\text{-dmnapy})(P(OC_6H_5)_3)$	Octane	1 hr	57.41	57.39	3.89	3.60	4.32	4.36
$Mo(CO)_3(2,7\text{-dmnapy})(P(OC_6H_4\text{-}p\text{--}CH_3)_3)$ [a]	Octane	4 hr	59.13	59.63	4.52	4.56	4.06	4.21
$Mo(CO)_3(2,7\text{-dmnapy})(DPDP)$ [a]	Octane	1 hr	51.07	51.31	4.46	4.52	4.96	5.13
$Mo(CO)_3(2,7\text{-dmnapy})(P(C_6H_5)_3)$	Octane	2 hr	62.00	62.37	4.20	4.15	4.66	4.89
$Mo(CO)_3(2,7\text{-dmnapy})(P(C_8H_{17})_3)$	Octane	2 hr	62.69	62.74	8.67	9.03	3.95	4.18
$Mo(CO)_3(2,7\text{-dmnapy})(As(C_6H_5)_3)$	Xylene	4 hr	57.77	57.81	3.91	3.95	4.35	4.58
$Mo(CO)_3(2,7\text{-dmnapy})((Sb(C_6H_5)_3)$	Xylene	4 hr	53.86	53.98	3.64	3.63	4.05	4.38
$Mo(CO)_3(2,9\text{-dmphen})(P(C_6H_5)_3)$	Octane	2 hr	64.62	64.69	4.18	4.21	4.31	4.57
$Mo(CO)_3(2,9\text{-dmphen})(P(OC_6H_5)_3)$	Octane	1 hr	60.18	60.23	3.90	4.00	4.01	4.06
$Mo(CO)_2(2,7\text{-dmnapy})(P(C_6H_5)_3)_2$	Mesitylene	20 hr	69.06	69.15	4.83	4.84	3.36	3.57
$Mo(CO)_2(2,7\text{-dmnapy})(P(OC_6H_5)_3)_2$ [a]	Xylene	2 hr	61.93	61.84	4.33	4.17	3.01	3.21
$Mo(CO)_2(2,7\text{-dmnapy})(P(OC_6H_4\text{-}p\text{--}CH_3)_3)_2$ [a]	Mesitylene	4 hr	63.90	63.90	5.16	5.18	2.76	2.81
$Mo(CO)_2(2,7\text{-dmnapy})(DPDP)_2$	Xylene	14 hr	53.54	53.44	5.29	5.24	3.67	3.56
$Mo(CO)_2(2,7\text{-dmnapy})(P(O\text{-}i\text{-}C_3H_7)_3)_2$ [a]	Xylene	5 hr	49.58	49.30	7.21	7.16	3.85	3.87
$Mo(CO)_2(2,9\text{-dmphen})(P(C_6H_5)_3)_2$	Mesitylene	24 hr	70.59	70.58	4.78	4.67	3.17	3.36
$Mo(CO)_2(2,9\text{-dmphen})(P(OC_6H_5)_3)_2$	Xylene	2 hr	63.68	63.72	4.32	4.23	2.86	3.12

[a] Requires chromatography for purification.

precipitate formed. Carbon, hydrogen and nitrogen compositions were ascertained by combustion.

Spectral Measurements. The infrared spectra of the compounds obtained in Nujol Mulls, KBr and CsI pellets (4000-200 cm^{-1}) and saturated chloroform solutions (2200-1600 cm^{-1}) were recorded with a Perkin-Elmer Model 621 double beam grating spectrophotometer. The proton magnetic resonance spectra obtained in deutro-chloroform with tetramethylsilane as an internal standard were recorded using a Varian HA-100 Spectrophotometer.

Results and Discussion

All the complexes are black or dark maroon, fairly air stable (stability periods range from days to months), but decompose rapidly in solution. They are slightly soluble in common organic solvents and insoluble in aliphatic hydrocarbons and water. As the dielectric constant of the organic solvent increases, the solubility and stability of the complexes increases. Although Dobson and Houk note that $Mo(CO)_3(bipy)$ $P(C_6H_5)_3$ exhibits appreciable stability in solution,[13] $Mo(CO)_3$-$(2,7\text{-dmnapy})P(C_6H_5)_3$ is the most unstable of the compounds reported here.

A comparison of reaction times and temperatures for the formation of $cis\text{-}Mo(CO)_3(N\text{-}N)L$ from $Mo(CO)_4(N\text{-}N)$ and L (N-N = 2,7-dmnapy or 2,9-dmphen) with those of the analogous phen and bipy systems[14] suggests that the extent of labilization of the carbonyl groups *cis* to the bidentate ligand is similar for these four nitrogen heterocycles.[3] Previous investigators of

the reaction of $Mo(CO)_4(N\text{-}N)$ with L, where N-N is bipy,[15] 2,5-dithiahexane[2], N,N,N′,N′-tetramethylethylenediamine,[2] and L is a phosphite or a phosphine have observed that in addition to the formation of cis-$Mo(CO)_3(N\text{-}N)L$, the bidentate ligand can easily be replaced resulting in the formation of *cis* or *trans*-$Mo(CO)_4L_2$ and cis-$Mo(CO)_3L_3$. Studies on similar systems where N-N is phen[16] indicate exclusive formation of cis-$Mo(CO)_3(N\text{-}N)L$.

Employing the reaction conditions specified by Dobson and Houk for the formation of cis-$Mo(CO)_3(N\text{-}N)$-$P(OC_2H_5)_3$ and $cis,trans$-$Mo(CO)_2(N\text{-}N)(P(OC_2H_5)_3)_2$ where N-N is phen or bipy,[13] we observe facile and complete replacement of 2,7-dmnapy from $Mo(CO)_4$-$(2,7\text{-dmnapy})$. When the sterically demanding ligands such as phenyl and iso-propyl phosphites are employed instead of the n-alkyl ligands, the replacement of 2,7-dmnapy proceeds at a noticibly slower rate. To prepare the *cis, trans*-$Mo(CO)_2(N\text{-}N)L_2$ derivatives, it is essential to limit the amount of L to a 2 fold excess since higher concentrations of the bulky ligands produce a partial displacement of 2,7-dmnapy while complete replacement is produced by the less sterically demanding ligands. Although the products of these displacement reactions were not fully characterized, spectral evidence indicates that *cis*-, and *trans*-$Mo(CO)_3L_3$, *cis*- and *trans*-$Mo(CO)_4L_2$ are formed. Since 2,7-dmnapy and bipy possess the same pKa and similar π-bonding ability,[14] the difference in ease of replacement is most likely due to the difference in stability or four- and five-membered chelate systems.

The possible geometric isomers, point groups of each isomer, infrared active stretching modes and assign-

(13) L. W. Houk and G. R. Dobson, *J. Chem. Soc.*, (A), 317 (1966).
(14) L. W. Houk and G. R. Dobson, *Inorg. Chem.*, 5, 2119 (1966).

(15) J. R. Graham and R. J. Angelici, *J. Am. Chem. Soc.*, 87, 5590 (1965).
(16) J. R. Graham and R. J. Angelici, *Inorg. Chem.*, 6, 992 (1967)

Table II. Carbonyl Stretching Frequencies and Band Assignments

Compound	$A_{(1)}'$	$A_{(2)}'$	E	A"	Medium
Mo(CO)₃(2,7-dmnapy)P(OC₆H₅)₃	1945	1853		1811	CHCl₃
Mo(CO)₃(2,7-dmnapy)P(OC₆H₄—p—CH₃)₃	1942	1848		1810	CHCl₃
Mo(CO)₃(2,7-dmnapy)(DPDP)	1940	1846		1808	CHCl₃
Mo(CO)₃(2,7-dmnapy)P(OCH₂)₃CC₂H₅	1939	1843		1803	CHCl₃
Mo(CO)₃(2,7-dmnapy)P(OCH₃)₃	1933	1835		1793	CHCl₃
Mo(CO)₃(2,7-dmnapy)P(OC₂H₅)₃	1930	1831		1793	CHCl₃
Mo(CO)₃(2,7-dmnapy)P(O—n—C₄H₉)₃ ᵃ	1928	1830		1793	CHCl₃
Mo(CO)₃(2,7-dmnapy)P(O—i—C₃H₇)₃	1926	1826		1789	CHCl₃
Mo(CO)₃(2,7-dmnapy)P(C₆H₅)₃	1921	1817		1791	CHCl₃
Mo(CO)₃(2,7-dmnapy)As(C₆H₅)₃	1920	1819		1791	CHCl₃
Mo(CO)₃(2,7-dmnapy)P(n—C₄H₉)₃ ᵃ	1914	1809		1782	CHCl₃
Mo(CO)₃(2,7-dmnapy)P(n—C₈H₁₇)₃	1914	1808		1782	CHCl₃
Mo(CO)₃(2,7-dmnapy)Sb(C₆H₅)₃	1913	1803		1792	Mull
Mo(CO)₃(2,7-dmnapy)CH₃CN	1912		1790		CH₃CN
Mo(CO)₃(2,7-dmnapy)NC₅H₅	1906		1778		C₅H₅N
Mo(CO)₃(2,7-dmnapy)NC₅H₄—3—CH₃	1908		1777		CH₂Cl₂
Mo(CO)₃(2,7-dmnapy)NC₅H₄—2—NH₂	1905		1777		C₅H₅N
Mo(CO)₃(2,7-dmnapy)NC₅H₄—3—NH₂	1898	1792		1769	Mull
Mo(CO)₃(2,7-dmnapy)HCON(CH₃)₂	1896	1778		1754	Mull
Mo(CO)₃(2,9-dmphen)P(OC₆H₅)₃	1939	1849		1803	CHCl₃
Mo(CO)₃(2,9-dmphen)P(C₆H₅)₃	1916	1818		1787	CHCl₃

Compound	A₁	B₁			Medium
Mo(CO)₂(2,7-dmnapy)(P(OC₆H₅)₃)₂	1874	1790			CHCl₃
Mo(CO)₂(2,7-dmnapy)(P(OC₆H₄—p—CH₃)₃)₂	1870	1787			CHCl₃
Mo(CO)₂(2,7-dmnapy)(DPDP)₂	1864	1778			CHCl₃
Mo(CO)₂(2,7-dmnapy)(P(O—i—C₃H₇)₃)₂	1822	1739			CHCl₃
Mo(CO)₂(2,7-dmnapy)(P(C₆H₅)₃)₂	1809	1731			CHCl₃
Mo(CO)₂(2,9-dmphen)(P(OC₆H₅)₃)₂	1870	1788			CHCl₃
Mo(CO)₂(2,9-dmphen)(P(C₆H₅)₃)₂	1805	1728			CHCl₃

ᵃ Although identified in solution by their spectra, isolation as pure substances was not possible.

ments of these modes to observed carbonyl vibrations in analogous systems have been discussed elsewhere.[4] Based on these discussions, we have assigned the *cis* configuration to the Mo(CO)₃(N-N)L complexes and a *trans*-L₂ configuration to the Mo(CO)₂(N-N)L₂ complexes. A single methyl resonance for the dimethyl heterocyclic bases in the pmr spectra substantiates the proposed geometries. Assignment of the carbonyl stretching modes to the observed carbonyl stretching vibrations are made in Table II.

For Mo(CO)₃(N-N)L compounds it has been proposed that as the π-bonding abilities of N-N and L become more dissimilar a greater splitting of the E mode will occur.[13] This may be viewed as the result of a change from *cis*-C₃ᵥ to a *cis*-Cₛ symmetry. The splitting of the E mode in complexes of Mo(CO)₃ (2,7-dmnapy)L, where L is a phosphite or phosphine, are consistently less by 1 to 4 cm⁻¹ than the analogous complexes of Mo(CO)₃(2,9-dmphen)L, Mo(CO)₃(phen)-L or Mo(CO)₃(bipy)L. Although many of the differences fall with the ±1 cm⁻¹ range of instrument reproducibility, the consistency of the differences suggests that if 2,7-dmnapy is not closer to phosphines in π-bonding ability than 2,9-dmphen, phen and bipy, then it is as least as great as the five-membered chelate systems. If one uses the position of the CO streching frequencies of analogous 2,7-dmnapy and 2,9-dmphen complexes as a measure of π-bonding ability, the same conclusion is reached. The shifts in CO stretching frequencies for the Mo(CO)₃(2,7-dmnapy)L compounds follow the accepted π-bonding order of the Lewis bases.[2,6,8] However, it should be noted that the CO positions conform equally well to

an inverse relationship with the pKa's of the Lewis bases.

Chemical shifts for 2,7-dmnapy and its complexes are presentend in Table III. The most striking feature of the pmr data is that with respect to the free ligands, all positions are shielded in the complex form. One might expect that complex formation *via* electron donation to the metal would produce deshielding of ligand protons as has been observed for R₂SnCl₂(2,7-dmnapy)[18], M(CO)₃(2,7-dmnapy)X where M is Mn or Re and X is Cl, Br or NO₃[19], M(2,7-dmnapy)₂²⁺ where M is Mg, Ca, Sr or Ba[20] and M(CO)₆₋ₓLₓ where M is Cr, Mo or W, x is 1-3 and L is a phosphite[21] or phosphine[22]. The magnitude of shielding of the heterocycle follows the order: tricarbonyl with alkyl phosphorus base < tricarbonyl with aryl phosphorus base < dicarbonyl complex. The shielding of the phosphites also increases on going from a tricarbonyl to a dicarbonyl compound. If the pmr behavior is interpreted as resulting from electron donation, one is forced to conclude that π-back donation > σ-donation. Instead, we propose that the large diamagnetic anisotropy produced by the L groups is the major contributor to the shielding of the heterocyclic protons. The ring currents of aryl groups of Lewis bases produce more shi-

(17) R. J. Angelici and Sr. M. D. Malone, *Inorg. Chem.*, 6, 1731 (1967).
(18) D. G. Hendricker, *Inorg. Chem.*, 8, 2328 (1969).
(19) D. G. Hendricker and J. R. Wagner, *Inorg. Chem.*, in press.
(20) R. L. Bodner and D. G. Hendricker, *Inorg. Chem.*, 9, 1255 (1970).
(21) W. E. Stanclift and D. G. Hendricker, *Inorg. Chem.*, 7, 1242 (1968).
(22) J. M. Jenkins, J. R. Moss, and B. L. Shaw, *J. Chem. Soc.*, (A), 2796 (1969).

Table III. Proton Magnetic Resonance Data[a]

Compound	4,5—H	3,6—H	2,7—CH₃	Chemical Shift Positions CH₃—	—CH₂—	C₆H₅—
2,7-napy	8.00	7.28	2.76			
Mo(CO)₃(2,7-napy)P(OCH₃)₃	7.99	7.32	2.70	3.46(3.51) [b]		
Mo(CO)₃(2,7-napy)P(OC₂H₅)₃	8.02	7.34	2.67	1.01(1.26)	3.85(3.87)	
Mo(CO)₃(2,7-napy)P(O—i—C₃H₇)₃	7.99	7.32	2.68	0.97(1.21)	1.03(1.28)	
Mo(CO)₃(2,7-napy)P(O—n—C₄H₉)₃	7.99	7.32	2.68	0.66(0.93)	1.34(1.56), 3.84(3.84)	
Mo(CO)₃(2,7-napy)P(n—C₄H₉)₃	7.99	7.32	2.69	0.79(0.91)	1.22(1.37)	
Mo(CO)₃(2,7-napy)P(n—C₈H₁₇)₃	7.98	7.32	2.96			
Mo(CO)₃(2,7-napy)P(OC₆H₅)₃	7.92	7.18	2.39			7.02(7.17)
Mo(CO)₃(2,7-napy)P(OC₆H₄—p—CH₃)₃	7.90	7.15	2.37	2.22(2.26)		6.84(702)
Mo(CO)₃(2,7-napy)(DPDP)	7.85	7.15	2.43	0.72(0.78)	1.34(1.30)	6.8 (7.09)
Mo(CO)₂(2,7-napy)(P(OC₆H₅)₃)₂	7.72	7.08	1.99			6.94(7.17)
Mo(CO)₂(2,7-napy)(P(OC₆H₄—p—CH₃)₃)₂	7.71	7.00	2.01	2.20(2.26)		6.78(7.02)
Mo(CO)₂(2,7-napy)(DPDP)₂	7.63	6.89	2.12	0.66(0.78)	1.28(1.30)	6.8 (7.09)

[a] Tetramethylsilane used as an internal reference in deuteriochloroform solutions for all spectra. [b] Values in parenthesis are for appropriate uncomplexed Lewis base.

elding of the 2,7-dmnapy protons that alkyl containing phosphorus donors, thus two groups of similar resonances are observed for Mo(CO)₃(2,7-dmnapy)L compounds. On proceeding from a tricarbonyl to a dicarbonyl compound, the shielding of the 2,7-CH₃ and 3,6-H are found to double while the 4,5-H shielding is tripled.

Replacement of a carbonyl group in Mo(CO)₃(2,7-dmnapy)L producing Mo(CO)₂(2,7-dmnapy)L₂ should result in enhanced back bonding to both L's over and above the amount available for back donation to L in the tricarbonyl complex. Indeed, the chemical shifts of the R groups of the phosphorus ligands are observed to be more shielded in the dicarbonyl than the tricarbonyl complex. If we assume that enhanced back bonding to L produces a slight decrease in the metal-phosphorus bond length, the L groups will be drawn nearer the naphthyridine chelate in the dicarbonyl complexes. That this assumption is reasonable is substantiated by the increase in ν M-P recorded on stepwise substitution of carbonyl groups by phosphite ligands.[23]

Since the shielding provided by phenyl groups is not symmetrical, but decreases drastically on aproaching the para position,[24] doubling the number of phenyl groups cis to the heterocycle would not be expected to double the shielding at all positions. In the tricarbonyl complexes, the 2,7-CH₃ and 3,6-H lie within the high shielding region while the 4,5-H are on the periphery of the phenyl ring currents. With closer approach of twice the number of phenyl groups in the dicarbonyl complexes, the 2,7-CH₃ and 3,6-H still lie within the same region of high ring current and are doubly shielded while the 4,5-H now are within, rather than on the periphery, and a triple shielding effect is observed.

(23) A. C. Vandenbroucke, Jr., D. G. Hendricker, R. E. McCarley, and J. G. Verkade, *Inorg. Chem.*, 7, 1825 (1968).

(24) C. E. Johnson, Jr., and F. A. Bovey, *J. Phys. Chem.*, 29, 1012 (1958).