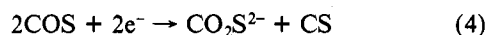$$2COS + 2e^- \rightarrow COS_2^{2-} + CO \qquad (3)$$
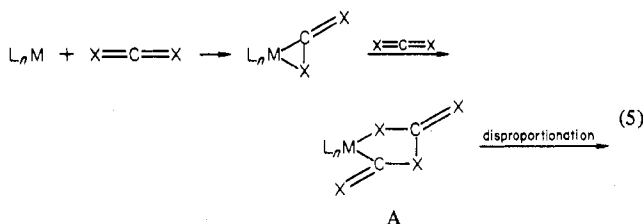
disproportionation paths of COS, the second one being reaction 4. Many cumulenes like CO_2,[2a] carbodiimides,[2b] and iso-

$$2COS + 2e^- \rightarrow CO_2S^{2-} + CS \qquad (4)$$

cyanates[3] undergo disproportionation in the reaction with metal complexes. The action of the metal is exemplified in (5). The

A

head-to-tail dimerization (A) of the functional group C=X seems to be the key intermediate preceding the disproportionation of the cumulene. It is rather difficult, however, to envisage such a mechanism for reaction 1, since when vanadocene reacts with functional groups like $-C\equiv C-$,[19] $>C=O$,[8] and $>C=N-$,[9] it forms 1:1 adducts only:

X = S; Y = S[20]
X = NR; Y = NR[22]
X = O; Y = CPh_2[19]
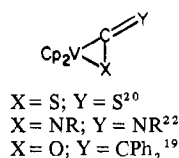
In the same studies we found that the nucleophilicity of the uncoordinated heteroatom (Y = S, NR) is rather high, so that its alkylation occurs with CH_3I under mild conditions.[9,21] On the basis of some considerations outlined above, we can propose the pathway shown by (6) for reaction 1.
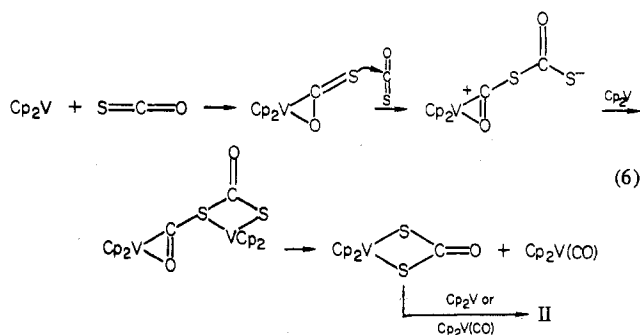
We must emphasize that COS is formally reduced by two electrons in its addition to the metal. The nucleophilic attack by the uncoordinated sulfur on the electrophilic carbon of another molecule of COS gives a head-to-tail linkage between two COS molecules, which is, probably, the prerequisite to the disproportionation.[24] A species like B may react with either $Cp_2V(CO)$ or Cp_2V to produce a vanadium derivative like II. Such a reaction was observed to occur between Cp_2VX_2 (X = Cl, SR) and Cp_2V.[25] The usual COS decomposition pathways cannot account for the formation of COS_2^{2-}.[26] While the disproportionation of CO_2 to CO_3^{2-} and CO is a well-established metal-promoted transformation,[2a] the generation of CS_3^{2-} from CS_2 is interpreted as occurring via the reaction of CS_2 on preformed metal–sulfido complexes.[27]

It can be noticed that, as suggested by this piece of vanadocene chemistry, the head-to-tail dimerization across two metal centers can account for the metal-induced disproportionation of cumulenes, including CO_2.[24]

(27) Benson, I. B.; Hunt, J.; Knox, S. A. R.; Oliphant, V. *J. Chem. Soc., Dalton Trans.* **1978**, 1240. Thiele, G.; Liehr, G.; Lindner, E. *J. Organomet. Chem.* **1974**, *70*, 427.

Molybdenum and Tungsten Complexes of Bidentate Bis(aryldiazenato) Ligands

Rino A. Michelin[1] and Robert J. Angelici*

As an extension of a study of the synthesis and reactivity of chelating bidentate nitrile and isocyanide ligands,[2] we report herein the preparation and chemical properties of potentially chelating bidentate bis(aryldiazenato) ligands of the structure

R = H, *t*-Bu
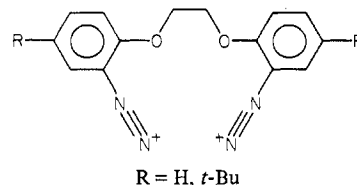
The ligands are abbreviated as DiN_2^{2+} (R = H) and *t*-Bu-DiN_2^{2+} (R = *t*-Bu). Molecular models indicate that these ligands should chelate best to octahedral or square-planar complexes where the angle between the donor groups is 90°. However, the formation of polymeric derivatives, owing to the flexibility of the alkyl chain, is also possible. To our knowledge, there are no reports in the literature of this type of ligand.

Recent interest[3] in aryldiazenato (ArN_2^+) ligands stems, in part, from studies of the similarities and differences of NO^+, N_2, and ArN_2^+. Only recently, several authors reported the syntheses, by different routes, of the rare complexes containing two aryldiazenato ligands.[4] The existence of these complexes suggested that derivatives containing the chelating DiN_2^{2+} and *t*-BuDiN_2^{2+} ligands could be prepared. It was toward this end that the following study was undertaken.

Experimental Section

General Procedures. All reactions involving organometallic compounds were carried out under an atmosphere of dry nitrogen.

(1) On leave of absence from the Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del CNR, Istituto di Chimica Industriale, 35100 Padua, Italy.
(2) Angelici, R. J.; Quick, M. H.; Kraus, G. A. *Inorg. Chim. Acta* **1980**, *44*, L137.
(3) Sutton, D. *Chem. Soc. Rev.* **1975**, *4*, 443.
(4) (a) Abel, E. W.; Burton, C. A.; Churchill, M. R.; Lin, K. G. *J. Chem. Soc., Chem. Commun.* **1974**, 352. (b) McCleverty, J. A.; Seddon, D.; Whitely, R. N. *J. Chem. Soc., Dalton Trans.* **1975**, 839. (c) Haymore, B. L. *J. Organomet. Chem.* **1977**, *137*, C11. (d) Butler, G.; Chatt, J.; Leigh, G. J. *J. Chem. Soc., Chem. Commun.* **1978**, 352. (e) Carroll, W. E.; Condon, D.; Deane, M. E.; Lalor, F. J. *J. Organomet. Chem.* **1978**, *157*, C58. (f) Connelly, N. G.; Gardner, C. *Ibid.* **1978**, *159*, 179.

(24) Duggan, M. D. *Inorg. Chem.* **1979**, *18*, 903. Herskowitz, T.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 1615. Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.*, in press.
(25) Fachinetti, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1974**, 2433.
(26) Hagen, A. P.; Callaway, B. W. *Inorg. Chem.* **1975**, *14*, 2825 and references cited therein.

Table I. IR and ¹HMR Spectroscopic Data for the Complexes

complex	IR,[a] cm⁻¹ ν(CO)	ν(NN)[b]	¹H NMR[c] (δ) Cp	CH_2CH_2	t-Bu	Ph	other
DiN₂[CpMo(CO)₂]₂ (Ia)	1987 s, 1902 s	1616 s, 1557 s	5.67 s	4.38 s		7.07–7.75 m	
t-BuDiN₂[CpMo(CO)₂]₂ (Ib)	1982 s, 1908 s	1612 s, 1547 s	5.70 s	4.34 s	1.32 s	7.04–7.91 m	
DiN₂[CpW(CO)₂]₂ (Ic)	1984 s, 1903 s	1610 s, 1548 s	5.81 s	4.39 s		6.45–7.70 m	
t-BuDiN₂[CpW(CO)₂]₂·0.5CH₂Cl₂ (Id)	1976 s, 1897 s	1607 s, 1543 s	5.81 s	4.35 s	1.32 s	7.00–7.85 m	5.29[d]
DiN₂[CpMo(PPh₃)(CO)]₂ (IIa)	1865 s	1511 s	5.31 s	4.26 s		6.86–7.36 m	
t-BuDiN₂[CpMo(PPh₃)(CO)]₂ (IIb)	1868 s	1510 s	5.27 s	4.21 s	1.28 s	6.83–8.12 m	
DiN₂[CpMo(N₂C₆H₄CH₃-p)(PPh₃)]₂(BF₄)₂[e] (IIIa)		1655 m, sh, 1621 s 1588 m, sh, 1560 s	6.28 d[f]	4.30 s		7.25–7.50 m	2.36 s, 2.30 s[g]
t-BuDiN₂[CpMo(N₂C₆H₄CH₃-p)(PPh₃)]₂(BF₄)₂[e] (IIIb)		1656 m, 1620 s 1582 m, 1549 s	6.02 d	4.12 s	1.38 s, 1.33 s	7.3–7.4 m	2.35 s, 2.31 s[g]

[a] Infrared spectra were run in dichloromethane solution; s = strong, m = medium, sh = shoulder. [b] Tentative assignment (see also text). [c] In CDCl₃ unless otherwise stated; s = singlet, d = doublet, m = multiplet. [d] Dichloromethane of crystallization. [e] ¹H NMR in CD₃CN. [f] Coupling constant J(Cp-P) $\simeq$ 1.0 Hz. [g] Methyl resonances of the p-tolyldiazonium group.

Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled under nitrogen from sodium benzophenone ketyl and LiAlH₄, respectively. Acetone was dried over CaSO₄ and degassed before use. All other solvents were of reagent grade purity and were dried over molecular sieves without further purification. IR spectra were taken on a Perkin-Elmer 281 spectrophotometer. Proton NMR spectra were recorded on a Hitachi Perkin-Elmer R-20B, JEOL FX-90Q, or Varian HA-100 instrument using tetramethylsilane (Me₄Si) as an internal standard. Melting points were taken on a Thomas hot-plate apparatus and are uncorrected.

Starting Materials. Na(C₅H₅) was prepared by a published procedure[5] by using DME instead of THF as solvent. A typical preparation of the CpM(CO)₃⁻ anions, where Cp = η^5-C₅H₅ and M = Mo or W, involved stirring of a slight excess of freshly redistilled cyclopentadiene collected at −78 °C and crystalline NaH in dry DME under N₂ at room temperature. After the evolution of H₂ had ceased (~2 h), to the solution was added a stoichiometric amount of the metal carbonyl M(CO)₆; the mixture was heated under N₂ at 90 °C for ~2 h (M = Mo) or 15 h (M = W) to yield the corresponding CpM(CO)₃⁻ anions. Other anions such as Mn(CO)₅⁻,[6] Co(CO)₄⁻,[6] and Mn(PPh₃)₂(CO)₃⁻[7] were prepared according to literature methods.

Preparation of Solid Diazonium Salts. The diazonium ligands were prepared by diazotization of the analogous diamines (DiNH₂ or t-BuDiNH₂) whose syntheses are described elsewhere.[2]

DiN₂²⁺(BF₄⁻)₂. To a suspension of DiNH₂ (3.05 g, 12.5 mmol) in 35 mL of distilled H₂O was added a 48% aqueous solution of HBF₄ (15 mL, ~105 mmol), and the mixture was cooled in an ice-water bath. A solution of KNO₂ (2.20 g, 25.8 mmol) in 10 mL of H₂O was added dropwise over a period of about 1–1.5 h, and then the mixture was stirred for another 1.5 h. The color gradually turned light pink during the reaction. The pink product was filtered from the mixture and washed with ice-cold water (3 × 15 mL), then with MeOH (6 × 20 mL), and finally with Et₂O (3 × 30 mL). It was dried under vacuum to yield 5.4 g or 98% (mp 181–183 °C). IR (characteristic peaks, Nujol mull): 2273 (s), 1601 (s), 1575 (s), 1050 (vs, br) cm⁻¹. ¹H NMR (CH₃CN): δ 4.87 (s, CH₂CH₂), 7.47–8.22 (m, Ph). Anal. Calcd for C₁₄H₁₂N₄O₂B₂F₈: C, 38.05; H, 2.74; N, 12.68. Found: C, 37.78; H, 2.74; N, 12.73.

t-BuDiN₂²⁺(BF₄⁻)₂. This compound was prepared in a similar way to that described above starting from t-BuDiNH₂ (2.85 g, 8.0 mmol), 48% aqueous HBF₄ (13 mL, ~90 mmol), and KNO₂ (1.40 g, 16.5 mmol). The white cream product was washed with ice-cold H₂O (3 × 15 mL), then with cold (0 °C) MeOH (20 mL), and finally with Et₂O (3 × 30 mL). It was dried under vacuum to yield 4.0 g or 90% (mp 182–184 °C dec). IR (characteristic peaks, Nujol Mull): 2260

(s), 1607 (m), 1559 (s), 1050 (vs, br) cm⁻¹. ¹H NMR (CD₃CN): δ 1.33 (s, t-Bu), 4.85 (s, CH₂CH₂), 7.5–8.25 (m, Ph). Anal. Calcd for C₂₂H₂₈N₄O₂B₂F₈: C, 47.68; H, 5.09; N, 10.11. Found: C, 47.83; H, 5.20; N, 10.29.

Preparation of Complexes. DiN₂[CpMo(CO)₂]₂ (Ia). To a stirred suspension of DiN₂²⁺(BF₄⁻)₂ (1.00 g, 2.26 mmol) in acetone (100 mL) at −78 °C was added a solution of CpMo(CO)₃⁻ (4.0 mmol) in DME (20 mL) via a cannula. The solution turned red and was stirred at the low temperature for 20 min. On slow warming of the solution to room temperature, an orange-red solid began to precipitate. The reaction mixture was stirred for an additional 2 h and then was filtered. The solid on the frit was treated with CH₂Cl₂ (80 mL), giving a dark red solution from which, on addition of MeOH (20 mL) and concentration under reduced pressure, a first crop of Ia precipitated as a red crystalline solid (0.24 g). The mother liquor was taken to dryness, and Et₂O (80 mL) was added. A brown solid was filtered from the mixture. This solid was extracted with CH₂Cl₂ (80 mL). Addition of MeOH (30 mL) and proceeding as above gave a second crop of Ia (0.36 g). The total yield was 0.60 g or 43% (on the Basis of Mo) (mp 175–178 °C dec (without melting)). Anal. Calcd for C₂₈H₂₂N₄O₆Mo₂: C, 47.88; H, 3.16; N, 7.98. Found: C, 47.73; H, 3.33; N, 7.80. IR and ¹H NMR data for this compound, as well as for the other organometallic complexes, are listed in Table I.

t-BuDiN₂[CpMo(CO)₂]₂ (Ib). The solution of CpMo(CO)₃⁻ (6.0 mmol) in DME was taken to dryness under reduced pressure, acetone (80 mL) was added, and the solution was cooled to −78 °C in a dry ice–acetone bath. Solid t-BuDiN₂²⁺(BF₄⁻)₂ (1.66 g, 3.0 mmol) was added in small portions over a period of a few minutes. After the addition was complete, the mixture was stirred at low temperature for 30 min, then slowly warmed to room temperature, and stirred for 2 h more. Then it was taken to dryness, and CH₂Cl₂ (80 mL) was added. The solution was filtered and evaporated to dryness. A filtered extract in CH₂Cl₂ (20 mL) was chromatographed on a 50 × 2 cm neutral alumina column with use of Et₂O as the eluant. The orange-red band was collected under N₂. Addition of pentane (40 mL) and cooling to −20 °C gave orange-red microcrystals (0.93 g, 38% yield) (mp 153–155 °C dec). Anal. Calcd for C₃₆H₃₈N₄O₆Mo₂: C, 53.08; H, 4.70; N, 6.88. Found: C, 53.46; H, 4.92; N, 6.68.

DiN₂[CpW(CO)₂]₂ (Ic). This compound was prepared in a manner analogous to that of Ia starting from CpW(CO)₃⁻ (3.1 mmol) and DiN₂²⁺(BF₄⁻)₂ (0.69 g, 1.55 mmol). Recrystallization from CH₂Cl₂/MeOH afforded 0.60 g or 44% yield of orange-red microcrystals (mp >150 °C (progressively decomposes without melting)). Anal. Calcd for C₂₈H₂₂N₄O₆W₂: C, 38.29; H, 2.53; N, 6.38. Found: C, 37.67; H, 2.71; N, 6.24.

t-BuDiN₂[CpW(CO)₂]₂·0.5CH₂Cl₂ (Id). This complex was prepared by a procedure similar to that used for Ib starting from CpW(CO)₃⁻ (2.0 mmol) and t-BuDiN₂²⁺(BF₄⁻)₂ (0.80 g, 1.44 mmol) in THF (80 mL). Recrystallization from CH₂Cl₂/pentane yielded orange-red crystals which were dried in vacuo (0.50 g, 57%) (mp >150 °C

(5) Greaves, W. W.; Angelici, R. J. *J. Organomet. Chem.* **1980**, *191*, 49.
(6) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553.
(7) Hieber, W.; Höfler, M.; Muschi, J. *Chem. Ber.* **1965**, *98*, 311.

(progressively darkens without melting)). Anal. Calcd for $C_{36}H_{38}N_4O_2W_2 \cdot 0.5CH_2Cl_2$: C, 42.44; H, 3.80; N, 5.42. Found: C, 42.43; H, 3.87; N, 5.38.

DiN$_2$[CpMo(PPh$_3$)(CO)]$_2$ (IIa). The complex Ia (0.70 g, 1.0 mmol) and PPh$_3$ (0.80 g, 3.05 mmol) were reacted in degassed methylcyclohexane (70 mL) by heating at 110 °C for 60 h. The orange solid which precipitated was filtered from the hot solution and washed several times with Et$_2$O. The yield was 0.93 g or 80% (mp 140–145 °C dec). This compound is light sensitive darkening progressively in several days and decomposing rapidly in solution.

***t*-BuDiN$_2$[CpMo(PPh$_3$)(CO)]$_2$ (IIb).** This compound was prepared by reacting Ib (0.35 g, 0.43 mmol) with PPh$_3$ (0.30 g, 1.1 mmol) in methylcyclohexane (40 mL) at 110 °C for 60 h. The hot mixture was filtered and the filtrate evaporated to dryness. A filtered extract of the residue in CH$_2$Cl$_2$ (15 mL) was chromatographed on neutral alumina (Fisher, activity grade 1, 80–200 mesh) eluting first with Et$_2$O to remove starting material. The orange band was then developed eluting with 1:1 CH$_2$Cl$_2$/Et$_2$O (v/v) and collected under N$_2$. Addition of hexane (20 mL) and slow evaporation of the solution under N$_2$ afforded an orange microcrystalline precipitate of IIb (0.32 g, 58% yield) (mp 126–128 °C dec). Anal. Calcd for $C_{70}H_{68}N_4P_2O_4Mo_2$: C, 65.52; H, 5.34; N, 4.36. Found: C, 65.00; H, 5.38; N, 4.18.

DiN$_2$[CpMo(N$_2$C$_6$H$_4$CH$_3$-*p*)(PPh$_3$)]$_2$(BF$_4$)$_2$ (IIIa). To a suspension of IIa (0.30 g, 0.25 mmol) in acetone at −78 °C was added [*p*-CH$_3$C$_6$H$_4$N$_2$][BF$_4$] (0.105 g, 0.51 mmol) in one portion. The dry ice–acetone bath was removed, and the reaction mixture was allowed to come slowly to room temperature and was stirred for an additional 3 h. The purple solution was taken to dryness, and CH$_2$Cl$_2$ (50 mL) was added. After filtration, the addition of Et$_2$O (80 mL) gave IIIa as a purple solid (0.29 g or 76% yield) (mp 140–145 °C dec).

***t*-BuDiN$_2$[CpMo(N$_2$C$_6$H$_4$CH$_3$-*p*)(PPh$_3$)]$_2$(BF$_4$)$_2$ (IIIb).** This compound was prepared by a procedure analogous to that for IIIa starting from IIb (0.18 g, 0.14 mmol) and [*p*-CH$_3$C$_6$H$_4$N$_2$][BF$_4$] (0.061 g, 0.30 mmol). Recrystallization from CH$_2$Cl$_2$/Et$_2$O gave IIIb as a dark purple solid (0.19 g or 83% yield) (mp 153–155 °C dec). Anal. Calcd for $C_{82}H_{82}N_8O_2P_2B_2F_8Mo_2$: C, 60.09; H, 5.04; N, 6.84. Found: C, 59.96; H, 5.21; N, 6.68.

Results and Discussion

The diazotization of 1,2-bis(2-amino-4-R-phenoxy)ethane[2] (abbreviated as DiNH$_2$, R = H, or *t*-BuDiNH$_2$, R = *t*-Bu) with KNO$_2$ in aqueous solution in the presence of HBF$_4$ gave, in excellent yield, the corresponding white bis(aryldiazonium) salts, DiN$_2^{2+}$(BF$_4^-$)$_2$ and *t*-BuDiN$_2^{2+}$(BF$_4^-$)$_2$. The ligands have been characterized by IR, ^{1}H NMR, and elemental analysis. They are stable in the solid state, and no decomposition is observed after storage under N$_2$ at 0 °C for several months. They are slightly soluble in acetone and acetonitrile, giving unexpectedly orange solutions from which, upon addition of Et$_2$O, orange crystalline solids can be isolated. The proton NMR spectra of these solids are identical with those of the crude white products. Since the orange compounds give correct C, H, and N analyses for the diazonium salts, the orange impurity must be present at very low concentrations.

It was of interest to examine the coordination properties and, in particular, the chelating abilities of the DiN$_2^{2+}$ and *t*-BuDiN$_2^{2+}$ ligands in reactions with transition-metal complexes which are known to form stable bis(aryldiazenato) derivatives. If the M–N–N–Ar array is linear, as it presumably is in the related nitrile and isocyanide ligands, chelation by DiN$_2^{2+}$ and *t*-BuDiN$_2^{2+}$ would be favored when the N$_2^+$ donor groups are at a 90° angle with respect to each other. However, all reported structures[3,9] of aryldiazenato complexes show that the N–N–Ar angle is roughly 120°, in which case the geometries of DiN$_2^{2+}$ and *t*-BuN$_2^{2+}$ would be less favorable for chelation.

The complexes CpMo(N$_2$Ar)(CO)$_2$, which were first synthesized by King and Bisnette[8] by reaction of the CpMo(CO)$_3^-$ anion with diazonium salts ArN$_2^+$, react as recently reported by Lalor and co-workers[4e] with another molecule of $^+$N$_2$Ar′ in the presence of PPh$_3$ or halide anion to give the cationic [CpMo(N$_2$Ar)(N$_2$Ar′)(PPh$_3$)]$^+$ or neutral CpMo-

Scheme I. Synthetic Scheme of Possible Reactions of Bis(aryldiazenato) Ligands[a]
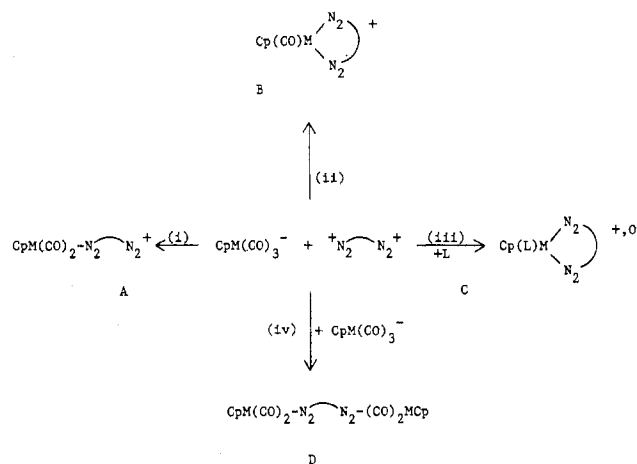
^{a} $^+$N$_2$N$_2^+$ = DiN$_2^{2+}$(BF$_4^-$)$_2$ or *t*-BuDiN$_2^{2+}$(BF$_4^-$)$_2$. L = tertiary phosphine or halide anion.

(N$_2$Ar)(N$_2$Ar′)X complexes, containing two terminally bonded diazonium groups. These complexes probably adopt a "three-legged" stool geometry similar to that of CpW-(N$_2$CH$_3$)(CO)$_2$[9] in which the three donor groups of the base are at right angles to each other. It, therefore, seemed that this system would be favorable for the synthesis of chelated DiN$_2^{2+}$ and *t*-BuDiN$_2^{2+}$ complexes.

Although the reactions of DiN$_2^{2+}$ and *t*-BuDiN$_2^{2+}$ with CpM(CO)$_3^-$ (M = Mo, W) anions could give the desired chelated products, there are four possible pathways that these reactions could follow (Scheme I): (i) formation of a monodentate monometallic compound A in which only one N$_2^+$ moiety is coordinated to the metal atom, (ii) formation of monometallic B in which the organic ligand is bidentate and chelated, (iii) formation of C by reaction with a ligand L such as a phosphine or halide anion, or (iv) formation of a bidentate binuclear D in which the ligand acts as a bridge between two metal atoms.

The path involving D seems to be definitely preferred. We were not successful in isolating an intermediate of type A, even by adding dropwise the metal anion to a dilute solution of an equivalent amount of the ligand; neither did this reaction afford a complex of type B. This latter result is not surprising because complexes having a carbonyl and two diazonium groups bonded to the metal were also not isolated by using monodentate diazonium ligands, although they had been postulated as labile intermediates in subsequent reactions with ligands, L.[4e] It is noteworthy that, in our case, addition at low temperature of PPh$_3$ or [PPN][Cl] to the reaction mixtures also did not provide any complexes of type C. In all of these reactions, complexes of type D were isolated, indicating that the reaction leading to a bidentate binuclear complex is, in this case, favored over other competing reactions.

The structures of these binuclear complexes have been established by IR, ^{1}H NMR (see Table I), and analytical data (see Experimental Section). The red-orange complexes I are moderately air stable and slightly light sensitive; they are best stored under nitrogen or in vacuum-sealed tubes in the dark. They are generally soluble in chlorinated solvents and insoluble in saturated hydrocarbons. As a general feature, compounds containing the *t*-BuDiN$_2^{2+}$ ligand are much more soluble than those of DiN$_2^{2+}$. They are stable in solution for several hours at room temperature, after that gradually decomposing to

(8) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1966**, *5*, 300.

(9) Hillhouse, G. L.; Haymore, B. L.; Herrmann, W. A. *Inorg. Chem.* **1979**, *18*, 2423.

brown solids. The IR spectra of I show two strong $\nu(CO)$ stretching frequencies in the range 1900–2000 cm^{-1} and two $\nu(NN)$ bands of medium to strong intensity between 1550 and 1615 cm^{-1} which are probably coupled with the vibrational modes of the attached phenyl groups.[10] Proton NMR spectra show the expected cyclopentadienyl and ligand signals.

The compounds I are similar in chemical behavior to the mononuclear analogues CpMo(N$_2$Ar)(CO)$_2$.[8] They react with PPh$_3$ in boiling methylcyclohexane to afford the corresponding orange substituted products DiN$_2$[CpMo(PPh$_3$)(CO)]$_2$ (IIa) and *t*-BuDiN$_2$[CpMo(PPh$_3$)(CO)]$_2$ (IIb) whose IR spectra show only one $\nu(CO)$ absorption at $\sim$1865 cm^{-1} and one strong $\nu(NN)$ vibration around 1510 cm^{-1}. Compounds IIa and IIb rapidly react with monodentate diazonium ligands such as [*p*-CH$_3$C$_6$H$_4$N$_2$][BF$_4$] in acetone at −78 °C to give the corresponding purple bis(aryldiazenato) complexes DiN$_2$-[CpMo(N$_2$C$_6$H$_4$CH$_3$-*p*)(PPh$_3$)]$_2$(BF$_4$)$_2$ (IIIa) and *t*-Bu-DiN$_2$[CpMo(N$_2$C$_6$H$_4$CH$_3$-*p*)(PPh$_3$)]$_2$(BF$_4$)$_2$ (IIIb), which show no $\nu(CO)$ absorptions in their IR spectra but exhibit four bands between 1550 and 1655 cm^{-1} in the $\nu(NN)$ region. In their proton NMR spectra, the methyl group signals of the *p*-tolyl ligands of IIIa and IIIb and the *tert*-butyl group signals of IIIb appear as two lines with intensity ratios of approximately 60:40. This observation may be tentatively explained by considering the chiral centers at the two molybdenum atoms, giving rise to a mixture of meso and *d,l* diastereomers. These two diastereomers would account for the NMR observations.

The complexes III could also be obtained by reactions of CpMo(N$_2$C$_6$H$_4$CH$_3$-*p*)(PPh$_3$)(CO) with DiN$_2$$^{2+}$ or *t*-Bu-DiN$_2$$^{2+}$ in acetone at −78 °C. Such reactions, however, did not provide any evidence for the formation of chelated complexes of the type [CpMo(DiN$_2$ or *t*-BuDiN$_2$)(PPh$_3$)]$^+$ resulting from the displacement of the carbonyl and *p*-tolyldiazonium groups. The metathesis reaction between the *t*-Bu-DiN$_2$$^{2+}$ ligand and the coordinated *p*-tolyldiazonium groups in the complex [CpMo(N$_2$C$_6$H$_4$CH$_3$-*p*)$_2$(PPh$_3$)]$^{+}$ [4e] also did not take place even after several days' stirring in acetone at room temperature.

In an attempt to explore further the possibility of preparing chelate complexes of DiN$_2$$^{2+}$, other metal carbonyl anions were reacted with this ligand. The reactions of Mn(PPh$_3$)$_2$(CO)$_3$$^-$, Mn(CO)$_5$$^-$, and Co(CO)$_4$$^-$ with DiN$_2$$^{2+}$ at low temperature (−78 °C) gave deeply colored solutions; however, no characterizable products containing the N$_2$ moiety could be isolated after warming of the reaction mixtures to room temperature. Only in the case of the reaction between Co(CO)$_4$$^-$ and DiN$_2$$^{2+}$ at −78 °C in the presence of triphenylphosphine was an unstable product having $\nu(CO)$ at 2000 (s) and 1955 (s, br) cm^{-1} and $\nu(NN)$ at 1693 (m) and 1645 (sh) cm^{-1} in dichloromethane solution observed. The similarity of its IR data and chemical behavior to that of Co(N$_2$Ph)(PPh$_3$)(CO)$_2$[11] suggests that this compound is of the type DiN$_2$[Co(PPh$_3$)-(CO)$_2$]$_2$ in which the organic aryldiazenato ligand bridges the two Co atoms.

Reactions of the potentially chelating bidentate aryldiazenato ligands with the anionic metal complexes investigated so far seem to indicate that, unlike the related isocyanide and nitrile ligands, these prefer to bridge two metal centers rather than chelate to one. This may be due to the less favorable geometry resulting from a bent N–N–Ar geometry or other factors.

Contribution from the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Synthesis and Metal Carbonyl Complexes of *cis,cis*-1,3,5-Triisocyanocyclohexane, an Unusual Tridentate Ligand

Rino A. Michelin[1] and Robert J. Angelici*

Relatively little is known about the coordination chemistry of multidentate isocyanide ligands as compared to their monodentate analogues.[2] The synthesis and reactions of a series of alkyl[3-5] and aryl[6] diisocyanide ligands were recently investigated. We wish to report herein the synthesis and chemical properties of an unusual tridentate triisocyanide ligand, *cis,cis*-1,3,5-triisocyanocyclohexane (triNC), which is potentially capable of coordinating to a triangular array of three metal–metal-bonded atoms. The ligand may assume either of two forms: A or B. In form A the NC groups are

A   B

triNC
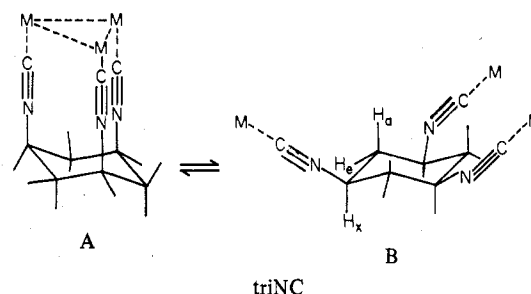
all axial and the three carbon atoms describe an equilateral triangle whose edge is about 2.5 Å. Molecular models indicate that this distance is comparable to metal–metal bond lengths in triangular arrays of metal atoms in many metal carbonyl clusters. Form A of triNC is related to the bidentate 1,3-diisocyanopropane (bridge) ligand which is known to bridge two interacting Rh atoms in the Rh$_2$(bridge)$_4$$^{2+}$ complexes.[3] These considerations suggested that triNC may be capable of coordinating to and perhaps stabilizing triangular arrays of metal atoms in simple M$_3$ clusters or in larger polyhedra with triangular faces.

(1) On leave of absence from the Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del CNR, Istituto di Chimica Industriale, 35100 Padua, Italy.
(2) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21.
(3) Lewis, N. S.; Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 7461.
(4) Kawakami, K.; Okajima, M.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2327.
(5) Yaneff, P. V.; Powell, J. *J. Organomet. Chem.* **1979**, *179*, 101.
(6) Angelici, R. J.; Quick, M. H.; Kraus, G. A. *Inorg. Chim. Acta* **1980**, *44*, L137.

(10) (a) Carroll, W. E.; Deane, M. E.; Lalor, F. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1837. (b) Sutton, D. *Can. J. Chem.* **1974**, *52*, 2634. (c) Haymore, B. L.; Ibers, J. A.; Meek, D. W. *Inorg. Chem.* **1975**, *14*, 541.
(11) Carroll, W. E.; Lalor, F. J. *J. Organomet. Chem.* **1973**, *54*, C37.