

perpendicular components [ $g_{\parallel} = 1.918$ ,  $g_{\perp} = 1.937$ ,  $a_{\parallel} = 81.3$  G,  $a_{\perp} = 33.2$  G] at room temperature. The isotropy of the esr spectrum of  $\text{PMo}_{12}\text{O}_{40}^{4-}$  indicates therefore that the unpaired electron in this complex is still very mobile even at  $6^{\circ}\text{K}$ .

The above results are consistent with a model for the electron structures of heteropoly blues in which the valence electrons oscillate between a number of metal atoms in identical sites. To a large extent the electron delocalization appears to be thermally activated.<sup>7</sup> Although further discussion of delocalization processes in heteropoly blues is beyond the scope of this communication, we note that the theoretical model of Hush<sup>8</sup> would predict an activation energy for thermal delocalization that is much too large (*ca.* 6 kcal/mol) to account for the degree of trapping observed here.

**Acknowledgment.** We thank the National Science Foundation and (in part) the Air Force Office for Scientific Research for support of this research through Grants GP-10538 and AF 70-1833, respectively.

(7) Laser irradiation of glassy samples at  $6328 \text{ \AA}$  during the esr measurements had no detectable effects on the spectra.

(8) N. S. Hush, *Progr. Inorg. Chem.*, **8**, 391 (1967). The activation energy is predicted to be 25% of the energy of the optical intervalence band which occurs at  $8000\text{--}10,000 \text{ cm}^{-1}$  in reduced molybdophosphate.

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### Keteneimmonium and 2-Azabutadiene Complexes from Reactions of $\alpha$ -Chloroenamines with Metal Carbonyl Anions

Sir:

$\alpha$ -Chloroenamines (I;  $\text{R} = \text{CH}_3$  or  $\text{R}_2 = (\text{CH}_2)_5$ ), unlike normal vinylic halides but like certain polycyano-vinyl halides,<sup>1</sup> are very reactive toward nucleophiles.<sup>2-4</sup> Reactions of these  $\alpha$ -chloroenamines (I) with various metal carbonyl anions<sup>5</sup> have now been found to yield new transition metal organometallic compounds including several species with novel structural features. In particular, the first transition metal complexes of keteneimmonium<sup>4,6</sup> and 2-azabutadiene systems have been prepared and characterized. The neutral unit  $(\text{CH}_3)_2\text{C}=\text{C}(\text{NR}_2)$  derived from the  $\alpha$ -chloroenamines has been found to bond to transition metals in five different ways: one way as a one-electron donor, three ways as a three-electron donor, and one way as a five-electron donor.

Some reactions of the  $\alpha$ -chloroenamines with metal carbonyl anions give relatively simple products in which the chlorine of the  $\alpha$ -chloroamine is replaced with a metal carbonyl residue. For example, reaction<sup>7</sup>

(1) R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **94**, 1784 (1972); **95**, 1811 (1973).

(2) L. Ghosez, B. Haveaux, and H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, **8**, 454 (1969).

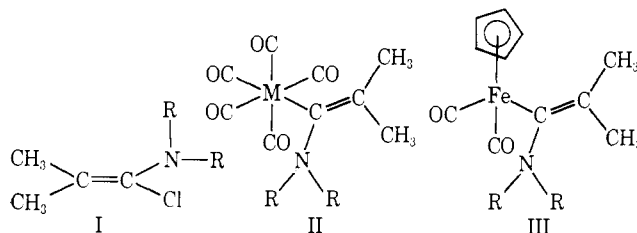
(3) M. Rens and L. Ghosez, *Tetrahedron Lett.*, 3765 (1970).

(4) J. Marchand-Brynaert and L. Ghosez, *J. Amer. Chem. Soc.*, **94**, 2869 (1972).

(5) R. B. King, *Accounts Chem. Res.*, **3**, 417 (1970).

(6) J. Marchand-Brynaert and L. Ghosez, *J. Amer. Chem. Soc.*, **94**, 2870 (1972).

(7) These reactions were carried out at ambient temperatures in the tetrahydrofuran solutions in which the metal carbonyl anions were prepared.



of  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{Cl}$  with  $\text{NaRe}(\text{CO})_5$  gives yellow crystalline<sup>8</sup>  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{Re}(\text{CO})_5$  (II;  $\text{M} = \text{Re}$ ,  $\text{R} = \text{CH}_3$ ): mp  $40\text{--}41^{\circ}$ ; infrared  $\nu(\text{CO})$  in hexane 2088 (m,  $\text{A}_1$ ), 2021 (w,  $\text{B}_1$ ), 1972 (vs, E), and  $1940 \text{ cm}^{-1}$ ; proton nmr<sup>9</sup> in  $\text{CDCl}_3$  [ $\text{N}(\text{CH}_3)_2$ ]  $\tau$  7.04 and  $[\text{C}(\text{CH}_3)_2]$  8.15 and 8.33. Reaction<sup>7</sup> of  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{Cl}$  with  $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$  gives air-sensitive brown liquid  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$  (III;  $\text{R} = \text{CH}_3$ ): infrared  $\nu(\text{CO})$  in hexane 2000 (s) and  $1949 \text{ cm}^{-1}$ ; proton nmr<sup>9</sup> in  $\text{CDCl}_3$  ( $\text{C}_5\text{H}_5$ )  $\tau$  5.31, [ $\text{N}(\text{CH}_3)_2$ ] 7.79, and  $[\text{C}(\text{CH}_3)_2]$  8.20 and 8.35. In these complexes the neutral  $(\text{CH}_3)_2\text{C}=\text{C}(\text{NR}_2)$  unit acts as a one-electron donor.

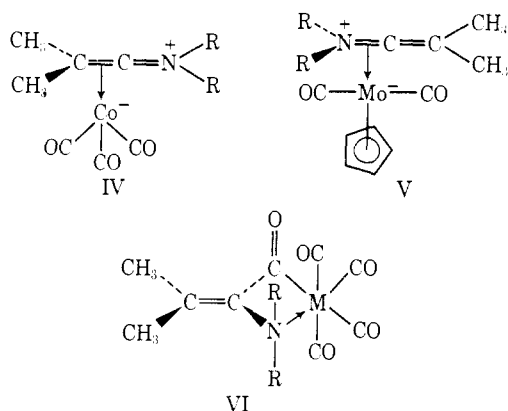
Two types of keteneimmonium transition metal complexes have been prepared from reactions of  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{Cl}$  with other metal carbonyl anions. Reaction<sup>7</sup> of  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{Cl}$  with  $\text{NaCo}(\text{CO})_4$  gives the air-sensitive yellow liquid<sup>8</sup>  $[(\text{CH}_3)_2\text{C}=\text{C}=\text{N}(\text{CH}_3)_2]\text{Co}(\text{CO})_3$ : bp  $30\text{--}35^{\circ}$  (0.5 mm) by evaporative distillation; infrared  $\nu(\text{CO})$  in hexane 2038 (s) and  $1961 \text{ cm}^{-1}$ ; proton nmr<sup>9</sup> in  $\text{CDCl}_3$  [ $\text{N}(\text{CH}_3)_2$ ]  $\tau$  6.63 and 6.79 and  $[\text{C}(\text{CH}_3)_2]$  8.46. Reaction<sup>7</sup> of  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{Cl}$  with  $\text{NaMo}(\text{CO})_3\text{C}_5\text{H}_5$  gives a 12% yield of yellow crystalline<sup>8,10</sup>  $[(\text{CH}_3)_2\text{C}=\text{C}=\text{N}(\text{CH}_3)_2]\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ : mp  $120\text{--}122^{\circ}$ ; infrared  $\nu(\text{CO})$  in  $\text{CH}_2\text{Cl}_2$  1930 (s) and  $1832 \text{ cm}^{-1}$ ; proton nmr<sup>9</sup> in  $\text{CDCl}_3$  ( $\text{C}_5\text{H}_5$ )  $\tau$  4.84, [ $\text{N}(\text{CH}_3)_2$ ] 7.38, and  $[\text{C}(\text{CH}_3)_2]$  8.10 and 8.14. In both of these compounds the neutral  $(\text{CH}_3)_2\text{C}=\text{C}=\text{N}(\text{CH}_3)_2$  unit acts as a three-electron donor. The distinct differences in the nmr spectra of the protons in the  $(\text{CH}_3)_2\text{C}=\text{C}=\text{N}(\text{CH}_3)_2$  units of the cobalt and molybdenum complexes suggest different modes of bonding of this three-electron ligand in the two complexes. If the geometry of the  $(\text{CH}_3)_2\text{C}=\text{C}=\text{N}(\text{CH}_3)_2$  ligand approximates that of tetramethylallene with a linear central sp carbon atom, postulation of structures IV ( $\text{M} = \text{Co}$ ,  $\text{R} = \text{CH}_3$ ) and V ( $\text{M} = \text{Mo}$ ,  $\text{R} = \text{CH}_3$ ) for these complexes can account for the nmr equivalence of the two C-methyl groups and the nmr nonequivalence of the two N-methyl groups in the cobalt complex as well as the nmr equivalence of the two N-methyl groups and the nmr nonequivalence of the two C-methyl groups in the molybdenum complex. These observations suggest that a keteneimmonium ligand such as  $(\text{CH}_3)_2\text{C}=\text{C}=\text{N}(\text{CH}_3)_2$  can bond to transition metals either through the carbon-carbon or the carbon-nitrogen double bond.

Cyclic acyl derivatives in which a carbonylated neutral  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{C}(\text{O})-$  unit acts as a three-electron donor have also been prepared. Reaction<sup>7</sup> of  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{Cl}$  with  $\text{NaMn}(\text{CO})_5$  gives a 60% yield of air-stable yellow crystalline<sup>8</sup>  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{C}(\text{O})\text{Mn}(\text{CO})_4$ : mp  $90\text{--}92^{\circ}$ ; infrared  $\nu(\text{CO})$  in

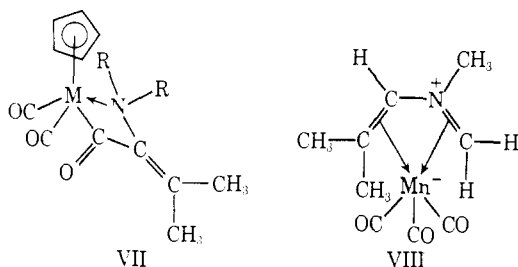
(8) These new compounds were characterized by correct elemental analyses for at least carbon, hydrogen, nitrogen, and oxygen.

(9) All of the resonances in these proton nmr spectra were singlets.

(10) The mass spectrum of this compound exhibited a molecular ion and ions corresponding to the stepwise loss of the carbonyl groups.



hexane 2071 (m), 1980 (s), 1964 (vs), 1953 (vs), and 1663 (m)  $\text{cm}^{-1}$ ; infrared  $\nu(\text{C}=\text{C})$  in KBr 1607  $\text{cm}^{-1}$ ; proton nmr<sup>9</sup> in  $\text{CDCl}_3$  [ $[\text{N}(\text{CH}_3)_2]$   $\tau$  6.85 and  $[\text{C}(\text{CH}_3)_2]$  8.09 and 8.33. These spectroscopic properties, particularly the observation of a *cis*- $\text{L}_2\text{M}(\text{CO})_4$  rather than an  $\text{LM}(\text{CO})_5$  pattern of terminal  $\nu(\text{CO})$  frequencies<sup>11</sup> and the presence of an acyl  $\nu(\text{CO})$  frequency (1663  $\text{cm}^{-1}$ ), preclude formulation of this manganese derivative as II ( $\text{M} = \text{Mn}$ ,  $\text{R} = \text{CH}_3$ ) analogous to the rhenium compound discussed above but instead require formulation as a cyclic acyl derivative such as VI ( $\text{M} = \text{Mn}$ ,  $\text{R} = \text{CH}_3$ ). Similarly, reaction<sup>7</sup> of  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{Cl}$  with  $\text{NaW}(\text{CO})_5\text{C}_5\text{H}_5$  gives a low yield of yellow crystalline<sup>8</sup>  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{C}(\text{O})\text{W}(\text{CO})_2\text{C}_5\text{H}_5$  (VII;  $\text{M} = \text{W}$ ,  $\text{R} = \text{CH}_3$ ): mp 106–112° dec; infrared  $\nu(\text{CO})$  in  $\text{CH}_2\text{Cl}_2$  1938 (s), 1913 (w), 1856 (s), 1822 (w), and 1617 (m)  $\text{cm}^{-1}$ ; proton nmr<sup>9</sup> in  $\text{CDCl}_3$  ( $\text{C}_5\text{H}_5$ )  $\tau$  4.80, [ $[\text{N}(\text{CH}_3)_2]$  6.44 and 6.76, and  $[\text{C}(\text{CH}_3)_2]$  8.96. The nmr equivalence of the two *N*-methyl groups ( $\text{R} = \text{CH}_3$ ) in  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{C}(\text{O})\text{Mn}(\text{CO})_4$  (VI) but their nonequivalence in  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{C}(\text{O})\text{W}(\text{CO})_2\text{C}_5\text{H}_5$  (VII;  $\text{M} = \text{W}$ ) arises from the symmetry of the *cis*- $\text{Mn}(\text{CO})_4$  unit and the asymmetry of the  $\text{W}(\text{CO})_2\text{C}_5\text{H}_5$  unit.



Ultraviolet irradiation of  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{C}(\text{O})\text{Mn}(\text{CO})_4$  (VI;  $\text{M} = \text{Mn}$ ,  $\text{R} = \text{CH}_3$ ) in hexane solution<sup>12</sup> results in the loss of two carbonyl groups to give a 28% yield of a yellow crystalline tricarbonyl:<sup>7,9</sup> mp 36–37°; infrared  $\nu(\text{CO})$  in hexane 2018 (s), 1927 (s), and 1906 (s)  $\text{cm}^{-1}$ . The proton nmr spectrum of this tricarbonyl indicates migration of one of the *N*-methyl protons to the carbon atom not bearing the methyl groups, resulting in the complex VIII with the five-electron donor 2-azabutadiene ligand. Thus, this proton nmr spectrum exhibits resonances at  $\tau$  4.66 (singlet), 7.40 (singlet), 8.01 (doublet,  $J = 5$  Hz), 8.16 (singlet), 8.27 (singlet), and 8.56 (broadened doublet,

(11) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

(12) This double decarbonylation reaction also proceeds without ultraviolet irradiation in boiling heptane or hexane; 13 days are required for completion in the latter solvent.

$J = 5$  Hz) of approximate relative intensities 1:3:1:3:3:1, respectively, which may be assigned to the  $-\text{CH}=\text{C}-$  proton, the *N*-methyl group, one  $=\text{CH}_2$  proton, the two nonequivalent *C*-methyl groups, and the other  $=\text{CH}_2$  proton, respectively. The hydrogen migration necessary to convert the manganese carbonyl derivative VI ( $\text{M} = \text{Mn}$ ,  $\text{R} = \text{CH}_3$ ) to the 2-azabutadiene manganese tricarbonyl derivative is somewhat similar to hydrogen migrations which occur upon heating iron carbonyls with nonconjugated diolefins<sup>13</sup> to give iron tricarbonyl complexes of conjugated diolefins.

Implicit in some of the above structural deductions through proton nmr spectroscopy is the assumption that the lower field methyl resonances arise from the *N*-methyl groups and the higher field methyl resonances arise from the *C*-methyl groups. This assumption has been verified by preparation, characterization, and taking the nmr spectra of the piperidino analogs of the key compounds IV, V, VI, and VIII (*i.e.*,  $2\text{R} = -(\text{CH}_2)_5-$ ) by reaction of the  $\alpha$ -chloroamine I ( $2\text{R} = -(\text{CH}_2)_5-$ ) with the corresponding metal carbonyl anion under conditions essentially identical with those used for the preparations of the dimethylamino analog (*i.e.*,  $\text{R} = \text{CH}_3$ ) discussed above.

This work indicates that reactions of  $\alpha$ -chloroamines with transition metal compounds can be used to prepare organometallic derivatives of novel types not yet obtainable by other methods. Further work on these interesting compounds is currently in progress.

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(13) R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961); J. E. Arnet and R. Pettit, *J. Amer. Chem. Soc.*, **83**, 2954 (1961); G. F. Emerson, J. E. Mahler, R. Kochhar, and R. Pettit, *J. Org. Chem.*, **29**, 3620 (1964).

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### Cationic Studies on the 9-Bicyclo[4.2.1]nona-2,4,7-trienyl System<sup>1,2</sup>

Sir:

An area of considerable research interest involves the nature of homoaromaticity<sup>3</sup> and bicycloaromaticity,<sup>4</sup> where the importance of these concepts was made evident by the chemical behavior of the 7-norbornadienyl and 7-norbornenyl cations.<sup>5</sup> The concept of bicyclo-

(1) This research was supported in part by the National Science Foundation, Cottrell Research Foundation, and USPHS 2-T01-GM-01045.

(2) Presented in part at the 8th Regional Meeting of the American Chemical Society, San Francisco, Calif., Oct 1972.

(3) See S. Winstein, *Chem. Soc., Spec. Publ.*, No. 21, 5 (1967); *Quart. Rev., Chem. Soc.*, **22** (2), 141 (1969).

(4) J. B. Grutzner and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2200 (1972); **92**, 3186 (1970); P. Alberg, J. B. Grutzner, D. L. Harris, and S. Winstein, *ibid.*, **92**, 3478 (1970).

(5) (a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4183 (1955); (b) A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133, 3135 (1966); (c) R. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **89**, 6350, 6352 (1967); (d) J. Lhomme, A. Diaz, and S. Winstein, *ibid.*, **91**, 1548 (1969).