

where bonding and antibonding MO's cross,⁵ this resulting from the one-electron degeneracy. As a consequence efficient conversion to ground state should occur.^{5,18}

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References and Notes

- (1) This is paper 91 of our photochemical series.
- (2) For paper 90 of the series, note H. E. Zimmerman and B. R. Cotter, *J. Amer. Chem. Soc.*, in press.
- (3) (a) H. E. Zimmerman, 17th National Organic Symposium, Bloomington, Ind., 1961, Abstracts; (b) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **83**, 4486 (1961); (c) *ibid.*, **84**, 4527 (1962); (d) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); (e) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *J. Amer. Chem. Soc.*, **90**, 4892 (1968).
- (4) L. Salem, *J. Amer. Chem. Soc.*, **96**, 3486 (1974), has presented correlation diagrams for these processes and has assigned configurations in terms of symmetries corresponding to our "circle-dot-y" notation. Interestingly, he has found that the ground state reactant curve leads to excited state of product with crossing of states.
- (5) (a) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564 (1966); (b) *ibid.*, **88**, 1566 (1966); (c) H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971); (d) *ibid.*, **5**, 393 (1972).
- (6) This point has been made more recently by Dewar, *et al.*,⁷ who has apparently overlooked some earlier literature.⁵ Thus, ref 5b pointed out that at points of degeneracy along a correlation diagram Jahn-Teller vibrations may be available and with the correct symmetry and geometry to enhance radiationless transition of excited states to ground states. The Jahn-Teller effect has been discussed in further detail in ref 5d with exploration of surfaces in the vicinity of crossing points. Similarly, that forbidden ground state reactions have characteristic nonbonding degeneracies and crossings has been noted several times as in ref 5c. Also overlooked was our point in ref 5b that the noncrossing rule is not inviolate.
- (7) M. J. S. Dewar, *et al.*, *J. Amer. Chem. Soc.*, **96**, 5240, 5242, 5244, 5246 (1974).
- (8) H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Amer. Chem. Soc.*, **96**, 439 (1974).
- (9) (a) G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **86**, 3197 (1964); (b) G. N. Lewis, T. T. Magel, and D. Lipkin, *J. Amer. Chem. Soc.*, **62**, 2975 (1940); (c) W. J. Potts, *J. Chem. Phys.*, **23**, 65 (1955); (d) S. Sharafy and K. A. Muszkat, *J. Amer. Chem. Soc.*, **93**, 4119 (1971).
- (10) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N.Y., 1965.
- (11) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963).
- (12) K. Sandros, *Acta Chem. Scand.*, **23**, 2815 (1969).
- (13) (a) Sandros' value of $\phi_{isc} = 0.81 \pm 0.04$ was chosen,¹² it will provide upper limits for ϕ_{isc} in compounds 4-8. The alternative literature value is $\phi_{isc} = 0.51 \pm 0.20$;^{13b} (b) W. Heinzlmann and K. Labhart, *Chem. Phys. Lett.*, **4**, 20 (1969).
- (14) (a) W. R. Dawson and J. L. Kropp, *J. Phys. Chem.*, **73**, 693 (1969); (b) J. L. Kropp, W. R. Dawson, and M. W. Windsor, *ibid.*, **73**, 1747 (1969).
- (15) (a) All of the 1-phenylcycloalkenes decayed as single falling exponentials, except **8** which decays as the sum of two falling exponentials at room temperature but as a single exponential at 77°K. We attribute the double decay to cis and trans excited singlets. The abnormally long lifetime of **8** (slower decay rate than the pattern of 4-7 would predict) is attributed to the increased hydrogen-hydrogen nonbonded interaction in this medium-sized ring, inhibiting the twist which allows the molecule to reach conformations from which decay is facile. That the cyclooctene is abnormally strained is shown by the heat of hydrogenation of cyclooctene which is considerably lower than that of cyclohexene or cycloheptene;^{15b} (b) R. W. Turner and W. R. Meador, *J. Amer. Chem. Soc.*, **79**, 4133 (1957).
- (16) (a) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969). (b) It should be recognized that presently we focus attention on one mode of decay which seems dominant, namely twisting. However, other molecular vibrations must interact in the decay process. Thus, for example, the slightly inverted rates of the four- and five-ring 1-phenylcycloalkenes (**4** and **5**) may result from more ready phenyl twisting in the four-ring case.
- (17) E. Evteth, *Chem. Phys. Lett.*, **3**, 122 (1969).
- (18) Note the discussion and review by J. Michl in "Chemical Reactivity and Reaction Paths," G. Klopman, Ed., Wiley, New York, N.Y., 1974, p.301, where such excited state-ground state "energy funnels" are considered. This was also discussed by J. Michl, 5th International IUPAC Photochemistry Symposium, Enschede, Holland, July 21-26, 1974.

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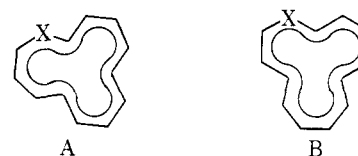
Effect of Heteroatom Electronegativity on the Development of Diatropic Character in *cis,trans,cis,trans,cis,trans*-Aza[13]annulenes

Sir:

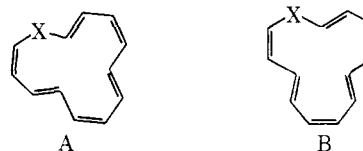
We recently reported on the title system, **1**, **2**, and stressed that whereas parent amine **1a**¹ is "aromatic" by nmr, acetamide **2a** and carbamate **2b** are best classed as polyenes under the same criterion.² Presently, we should like to briefly relate our experience with the conjugate base of **1a**, the *cis,trans,cis,trans,cis,trans*-aza[13]annuleny anion, as well as with three choice N-substituted derivatives whose properties yield basic information with regards to the skeletal and π -electronic effects controlling the development of "aromatic" character.

Potassium aza[13]annulene (**1b**) was generated for purposes of direct observation on overnight low-temperature (-78°) exposure of its conjugate acid (**1a**) to potassium mirror in THF-*d*₈. It is a dark red, extremely heat sensitive species rearranging cleanly and almost instantaneously to **3a** (nmr)³ on warming to 0°.⁴ As a result, it was necessary to record the nmr spectrum of **1b** at an undesirably low temperature (*ca.* -70°) with consequent loss of resolution due to increased medium viscosity. Nonetheless, one can still readily discern in this spectrum two well-separated doublets due to the α protons, one showing at τ 1.8 with $J \sim 7$ Hz ("outer" proton bound to a *cis* link) and the other appearing at τ 12.5 with $J \sim 13$ Hz ("inner" proton bound to a *trans* link). The wide separation (over 10 ppm!) between these two doublets is clearly implicative of the presence of a strongly diatropic frame in **1b**.

Next, we posed the question as to whether the system will retain its diatropic character when sterically encumbered with an electron-releasing N substituent such as methyl.⁵ The desired derivative, **1c**,⁶ was prepared on consecutive low-temperature (-78°) treatment of **1a** with methyl lithium and methyl iodide and was isolated as a yellow air-sensitive liquid characterized by the following spectral data: $\lambda_{max}(C_6H_{14})$ 300 and 360 nm in a ratio of *ca.* 7:1;⁷ nmr (100 MHz, acetone-*d*₆, 0°) τ 3.1-4.3 (9 H, m), 6.29 (1 H, dd, $J = 15.5, 9.0$ Hz; "inner" proton), 6.43 (3 H, s; meth-



1a, X = NH
b, X = $\ddot{N}K^+$
c, X = NMe



2a, X = NAc
b, X = NCOOMe
c, X = NCF=CF₂
d, X = NCON(Me)₂



3a, X = $\ddot{N}K^+$
b, X = NH

yl), 6.56 (1 H, dd, $J = 16.0, 11.0$ Hz; "inner" proton), 7.37 (1 H, d, $J = 14.0$ Hz; "inner" α proton); m/e 185 (P^+ ; 8%). The molecule is clearly diatropic by nmr experiencing strong shielding of all its "inner" hydrogens. In fact judging from the appearance of the "inner" hydrogen triad (τ 6.29, 6.56, and 7.37) at detectably higher fields than its counterpart in the spectrum of **1a** (τ 5.99, 6.52, and 7.22),² we find it tempting to pronounce **1c** more extensively delocalized than the parent (**1a**). Also interesting in this connection is the significant downfield shift of the methyl resonance of **1c** (τ 6.45) compared to its counterpart (τ 6.85) in the spectrum of the largely atropic nine-membered ring relative, *N*-methylazonine,⁸ which appears to reflect the larger member's reduction in heteroatom electron density due to more extensive delocalization of its lone pair.

For obvious electronic reasons we next became interested in the effect of the relatively "small" but intensely electron-withdrawing trifluoromethyl group. In practice, consecutive exposure of **1a** to methyllithium and trifluoromethyl iodide at -78° failed to yield the desired *N*-trifluoromethyl derivative but produced **2c** instead. When pure (sublimation), **2c** is a bright yellow solid displaying the following spectral characteristics: $\lambda_{\max}(\text{C}_6\text{H}_{14})$ 227, 278, and 334 nm in relative intensities of *ca.* 1.0:4.6:3.0; pmr (100 MHz, acetone- d_6 , $+2^\circ$) τ 3.3–4.0 (8 H, m), 4.18 (1 H, dd, $J = 14.5, 4.5$ Hz; β proton on trans bond), 4.43 (1 H, dd, $J = 15.5, 8.0$ Hz; "inner" proton), 4.59 (1 H, dd, $J = 16.0, 10.5$ Hz; "inner" proton), 5.30 (1 H, d,⁹ $J = 14.5$ Hz; "inner" α proton); fmr (94 MHz, acetone- d_6 , $\sim 35^\circ$)¹⁰ 143 (1 F, dd, $J = 112, 40$ Hz), 118 (1 F, dd, $J = 112, 71$ Hz), 105 (1 F, dd, $J = 71, 40$ Hz); m/e 251 (P^+ ; 100%). Obviously, there is detectable upfield shift of the "inner"-proton nmr signals (τ 4.43–5.30) relative to the major absorption manifold (τ 3.3–4.2). Nonetheless, the separation between the two is only barely perceptible so that the entire resonance manifold remains well within the region of the spectrum normally associated with unexceptional polyenes. The obvious conclusion then is that the electron-withdrawing $-\text{CF}=\text{CF}_2$ appendage exerts damaging influence on the system's ability to delocalize.

Finally, we undertook the task of introducing a weakly electron-withdrawing carbonyl substituent, namely the *N,N*-dimethylcarbamoyl group. The desired urea, **2d**, was prepared on successive low-temperature (-78°) exposure of **1a** to methyllithium and *N,N*-dimethylcarbamoyl chloride. It is a yellow crystalline solid (mp 54 – 55.5°) characterized by the following spectral data: $\nu_{\text{CO}}(\text{KBr})$ 1660 cm^{-1} , $\lambda_{\max}(\text{C}_6\text{H}_{14})$ 232 nm (ϵ 19,700), 280 (21,400), 350 (4900); nmr (100 MHz, CDCl_3) τ 3.4–4.3 (11 H, m), 4.50 (1 H, d, $J = 14.5$ Hz; "inner" α proton), 7.06 (6 H, s); m/e 242 (P^+ ; 8%). The molecule differs most conspicuously from its close relatives, **2a** and **2b**, by the clear upfield separation of its "inner" $-\text{H}_\alpha$ signal (doublet at τ 4.50) from the remainder of the spectrum. Nonetheless, here too, as in the case of **2c**, the shift is barely discernible so that the property (ring diamagnetism?) responsible for this phenomenon cannot be fully developed.

In sum, one finds the position of the H_α "inner" resonance in the nmr spectrum of a *cis,trans,cis,trans,cis,trans*-aza[13]annulene to constitute an effective measure of diatropic character clearly establishing the need for lone-pair participation in its development. Specifically, one witnesses the system's change from atropic in **2a** and **2b** to largely nondescript in **2c** and **2d** to diatropic in **1a** and **1c** and to more extensively so in **1b**, the difference in H_α "inner" chemical shift between the two extremes, **2a** and **1b** amounting to more than 8 ppm! Interestingly, a similar trend emerges from an examination of the system's uv char-

acteristics where the strong, second lowest energy, band in the spectrum is seen to undergo progressive bathochromic shift with decreasing heteroatom electronegativity, with the two extreme cases studied thus far, acetamide **2a** and *N*-methyl derivative **1c** differing by as much as 40 nm in this respect.

Finally, a brief word concerning the ready thermal conversion of **1b** to Schröder's anion **3a**. While the process might, at first glance, strike one as puzzling especially since amines **1a**² and **3b**³ are known not to interconvert on heating to *ca.* 50° , closer scrutiny yields a perfectly good explanation of the situation. Specifically, it is seen that while the hypothetical interconversion between **1a** and **3b** is predicted to occur with overall preservation of the number of interfering "inner" hydrogens, an "inner" C–H changing to an "inner" N–H on passing from **1a** to **3b** the observed transformation of anion **1b** to anion **3a** occurs with actual removal of a sterically offending proton; *i.e.*, here an "inner" C–H group is replaced by a *bare*, sterically innocuous, nitrogen function. In other words, we offer the suggestion here that geometrical isomerization among the diatropic aza-[13]annulenes occurs chiefly as a result of reduced "inner" proton repulsions, and, consequently, that Schröder's anion, **3a**, may well represent the true thermodynamic "sink" of the family.

Acknowledgment. We are grateful to the National Science Foundation (GP-38553X), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Department of Chemistry, Syracuse University, for support of this work. We are also indebted to Mr. Larry McCandless for the determination of the nmr spectra and to Dr. John A. Meyer of the College of Forestry, State University of New York at Syracuse, for extending this service to us. Dr. J. C. Concepcion's assistance in the preparation of the nmr sample of **1b** is also gratefully acknowledged.

References and Notes

- (1) In our original report on the subject we limited ourselves to the rotameric representation depicted under A. We now wish to offer B for consideration as well. In fact, judging from the nmr spectrum of **1a**, taken at ambient temperature, which shows clear signs of vicinal coupling between an "inner" proton and what is believed to be the β hydrogen (H_β) associated with the *cis* double bond directly adjacent to nitrogen, one may justifiably favor B as the most plausible rotameric representation of this substance at ambient temperature. Within this frame of reasoning the rotational mobility of this molecule, recently deduced from the "abnormal" temperature-induced pmr shifts of the *trans* bond whose pivotal motion is expected to interconvert A and B, may well be considered indicative of the molecule's preference for form A at the lower temperature.
- (2) A. G. Anastassiou and R. L. Elliott, *J. Amer. Chem. Soc.*, **96**, 5257 (1974).
- (3) G. Schröder, G. Frank, H. Röttele, and J. F. M. Oth, *Angew. Chem.*, **86**, 237 (1974). We are indebted to Professor Schröder for kindly supplying us with the nmr spectra of **3a** and **3b** for comparison purposes.
- (4) As expected, aqueous quench of lithium aza[13]annulene, generated from **1a** and methyllithium at -78° and then allowed to stir for several hours at 0° , yielded **3b** (nmr) rather than **1a**.
- (5) We were, of course, particularly interested in the question of *N*-methyl substitution because of our earlier findings and interpretations in connection with *N*-methylazonine, namely that the molecule is largely atropic because of serious steric congestion between the methyl group and its two adjacent α hydrogens.⁸ Obviously, no such congestion should be present in the (*ctctct*) skeleton shown in **1** so that the *N*-methyl derivative would be expected to have ready access to a flat frame and thus to be capable of sustaining ring diamagnetism.
- (6) In *N*-substituted derivatives with π -electronic affinity for a flat frame the steric congestion between *N*-substituent and *peri* hydrogen, *i.e.*, the β proton located on the *trans* bond, may well have a decisive influence on the choice of rotameric modification insofar as the two forms, A and B, are expected to greatly differ with regards to satisfying the spatial demands imposed by the substituent. Specifically, examination of "Dreiding" molecular models of **1c** reveals the minimum distance between methyl and *peri* hydrogen to be *ca.* 1.5 Å for rotamer A and *ca.* 1.9 Å for rotamer B amounting to H–H repulsions of *ca.* 25.5 and 9.5 kcal/mol, respectively! (see *e.g.*, H. E. Simmons, J. K. Williams, *J. Amer. Chem. Soc.*, **86**, 3222 (1964) and thus clearly favoring form B.)

- (7) The air sensitivity of the substance precluded a quantitative determination of extinction coefficients at this preliminary stage.
 (8) A. G. Anastassiou, S. W. Eachus, R. P. Cellura, and J. H. Gebrian, *Chem. Commun.*, 1133 (1970).
 (9) As expected, each component of this doublet appears as a finely split doublet of triplets.
 (10) Chemical shifts denote the *upfield* displacement (in ppm) of each resonance from that of the accepted standard, trichlorofluoromethane.
 (11) NDEA Graduate Fellow, 1971-1974.
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Synthesis and Structure of the Pentacarbonylmetalate Dianions of Chromium, Molybdenum, and Tungsten

Sir:

Systematic studies on the chemistry of the pentacarbonylmetalate dianions of Cr, Mo, and W have been hampered by the lack of facile syntheses.¹⁻⁵ Our desire to determine whether these dianions will be useful as stoichiometric reagents in organic syntheses and/or precursors to novel organotransition metal complexes has prompted us to examine new routes to these species. In this process general methods for the synthesis of these monomeric dianions have been discovered: the alkali metal reduction of $M(\text{CO})_6$, $M(\text{CO})_5(\text{halide})^-$, or $M_2(\text{CO})_{10}^{2-}$ in hexamethylphosphoramide (HMPA).

In 1968 it was reported that $\text{Cr}(\text{CO})_6$ was reduced by sodium metal in HMPA to give a substance formulated as " $\text{Cr}(\text{CO})_5\text{HMPA}^{2-}$ " on the basis of infrared spectra and sodium metal uptake.⁶ Under the same conditions as reported in this paper,⁶ we have obtained entirely different infrared spectra of the reduced chromium species in HMPA by using air-tight sodium chloride solution cells. Virtually identical spectra have also been obtained from analogous reductions of $M(\text{CO})_6$ ($M = \text{Mo}, \text{W}$), $M'_2(\text{CO})_{10}^{2-}$ ($M' = \text{Cr}, \text{Mo}, \text{W}$), and $M'(\text{CO})_5\text{X}^-$ ($X = \text{Cl}, \text{Br}, \text{I}$) in HMPA. Figure 1 shows various stages in the reduction of $\text{W}(\text{CO})_6$ in HMPA at room temperature. The principal intermediate in this reduction is $\text{W}_2(\text{CO})_{10}^{2-}$ which absorbs at 1939 (m), 1889 (vs), and 1790 cm^{-1} (s) in the carbonyl region. After approximately 4 hr all bands due to $\text{W}_2(\text{CO})_{10}^{2-}$ disappear; only bands at 1775 (vs) and 1731 cm^{-1} (vs) remain, which are attributed to $\text{Na}_2\text{W}(\text{CO})_5$.

Proof that the reduced chromium substance obtained in HMPA is identical with genuine $\text{Na}_2\text{Cr}(\text{CO})_5$, prepared by Behrens's method,² was provided by showing that HMPA solution spectra of substances made by both methods are identical. Further, by exposing HMPA solutions of $\text{Na}_2\text{Cr}(\text{CO})_5$ to air, spectra have been obtained which are virtually identical with that attributed to " $\text{Cr}(\text{CO})_5\text{HMPA}^{2-}$."⁷ Since we have shown that trace amounts of oxygen instantaneously convert $\text{Cr}(\text{CO})_5^{2-}$ to $\text{Cr}_2(\text{CO})_{10}^{2-}$, we believe that the species previously reported as " $\text{Cr}(\text{CO})_5\text{HMPA}^{2-}$ " is, in fact, mostly $\text{Cr}_2(\text{CO})_{10}^{2-}$.

Infrared spectra of $\text{Na}_2M(\text{CO})_5$ ($M = \text{Cr}, \text{Mo}$ and W) in HMPA (see Table I) show only two strong infrared active bands below 1800 cm^{-1} as expected for trigonal bipyramidal dianionic carbonyl species. Thus, little or no coordination of $M(\text{CO})_5^{2-}$ with the HMPA is indicated.⁸⁻¹⁰ Our spectra of $\text{Na}_2\text{Cr}(\text{CO})_5$ in tetrahydrofuran (THF) are in agreement with that reported recently by Behrens, *et al.*² Marked differences in the spectra of $\text{Na}_2\text{Cr}(\text{CO})_5$ in HMPA and THF are undoubtedly due to substantial ion pair formation in the latter solvent which effectively reduc-

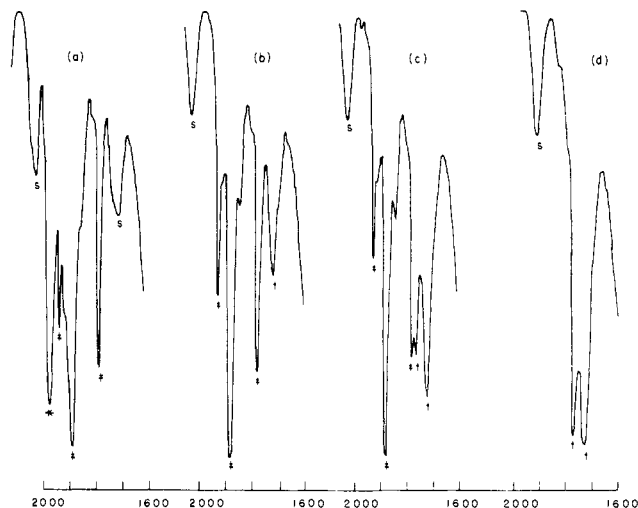


Figure 1. Infrared spectra showing the reduction of $\text{W}(\text{CO})_6$ by Na in HMPA at various times: (a) 1 hr, (b) 2.5 hr, (c) 3 hr, (d) 4 hr. Identity and positions of bands: s = HMPA; * = $\text{W}(\text{CO})_6$, 1973 cm^{-1} ; ‡ = $\text{W}_2(\text{CO})_{10}^{2-}$, 1938, 1889, 1789 cm^{-1} ; † = $\text{W}(\text{CO})_5^{2-}$, 1775, 1731 cm^{-1} .

Table I. Infrared Solution Spectra of Salts of $M(\text{CO})_5^{2-}$ in Carbonyl Stretching Frequency Region

Salt	Solvent	Carbonyl stretching frequencies (cm^{-1})
$\text{Na}_2\text{Cr}(\text{CO})_5$	HMPA	1760 (s), 1722 (s)
$\text{Na}_2\text{Cr}(\text{CO})_5$	THF	1819 (s), 1768 (s, br) ¹¹
$\text{Na}_2\text{Mo}(\text{CO})_5$	HMPA	1769 (s), 1723 (s)
$\text{Na}_2\text{W}(\text{CO})_5$	HMPA	1775 (s), 1731 (s)

es the symmetry of $\text{Cr}(\text{CO})_5^{2-}$ from D_{3h} in HMPA to approximately C_{4v} in THF.¹²⁻¹⁴ However, in contrast to their report that $\text{Cr}(\text{CO})_5^{2-}$ decomposes almost entirely to $\text{Cr}_2(\text{CO})_{10}^{2-}$ within 95 min in THF,² we find virtually no change in the spectra of THF solutions of $\text{Na}_2\text{Cr}(\text{CO})_5$ maintained under an atmosphere of moisture- and oxygen-free nitrogen for at least seven days.¹⁵ As mentioned previously, trace amounts of air instantaneously convert $\text{Cr}(\text{CO})_5^{2-}$ to $\text{Cr}_2(\text{CO})_{10}^{2-}$; the latter is characterized by a strong absorption in THF at 1890 cm^{-1} .¹⁶

The chemical properties of the pentacarbonylmetalate dianions are under study. They react with a variety of main-group and transition metal halides to generate products of the general formula $M(\text{CO})_5\text{E}^-$ by simple halide displacement. An account of this chemistry will be published in the near future.

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References and Notes

- Approximately 95% yields of $\text{Na}_2\text{Cr}(\text{CO})_5$ have been obtained by Na reduction of $\text{Cr}(\text{CO})_6$ in ammonia.² However, analogous reductions of molybdenum and tungsten hexacarbonyls provide only poor yields of the monomeric dianions, contaminated with other salts.³ Small quantities of pure $\text{Na}_2M(\text{CO})_5$ ($M = \text{Mo}, \text{W}$) are obtained by the disproportionation of $\text{Na}_2M_2(\text{CO})_{10}$ above 130° under a carbon monoxide atmosphere in a sealed tube. The latter is a technically difficult synthesis, useful for preparing only small amounts of the dianions.^{4,5}
- E. Lindner, H. Behrens, and D. Uhlig, *Z. Naturforsch. B*, **18**, 276 (1973).
- H. Behrens and R. Weber, *Z. Anorg. Allg. Chem.*, **291**, 122 (1957).
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- H. Behrens and J. Vogl, *Chem. Ber.*, **96**, 2220 (1963).
- W. C. Kaska, *J. Amer. Chem. Soc.*, **90**, 6340 (1968).