1,3-Dipolar Cycloaddition Reactions of Low-Valent Metal-Carbonyl Complexes with Arylnitrile *N*-Oxides

John A. Walker, Carolyn B. Knobler, and
M. Frederick Hawthorne*

Department of Chemistry and Biochemistry
University of California, Los Angeles, California 90024

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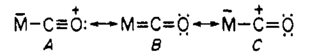
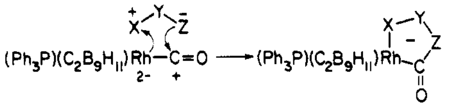
Recently chemists have begun to recognize and exploit isolobal[1a] relationships of C=C and M=C moieties. For example, Stone and co-workers have used this apparent bonding analogy to generate many heteronuclear metal clusters from zerovalent platinum reagents or other low-valent metal species and Fischer-type carbenes and carbynes.[1b] While these studies have focused on well-defined metal-carbon multiple bonds, another class of metal complexes generally believed to contain metal-carbon multiple-bond character,[2] the low-valent metal-carbonyl complexes, has not received similar attention. We report here a new reaction involving this incipient M=C bond.

Bonding in metal carbonyl complexes can be qualitatively described by A–C. Structures A and C, which do not involve



$$\underset{A}{\bar{\mathrm{M}}-\mathrm{C}\equiv\overset{+}{\mathrm{O}}:} \longleftrightarrow \underset{B}{\mathrm{M}=\mathrm{C}=\ddot{\mathrm{O}}} \longleftrightarrow \underset{C}{\bar{\mathrm{M}}-\overset{+}{\mathrm{C}}=\ddot{\mathrm{O}}}$$

back-bonding, suggest the presence of a nucleophilic metal atom and an electrophilic carbon atom, which when employed together, might lead to reactions of certain metal-carbonyl complexes with 1,3-dipolar molecules. Optimally, an electron-rich metal carbonyl complex capable of increasing its coordination number from five to six would be expected to be particularly reactive. The two isomeric rhodacarborane anions $[(Ph_3P)(CO)RhC_2B_9H_{11}]^-$ (**1a**, 3,1,2-isomer; **1b**, 2,1,7-isomer), reported in the preceding communication,[3] possess the key electronic and structural features necessary for such a [3 + 2] cycloaddition reaction, viz., eq 1.



(1)

Indeed the classical 1,3-dipolar molecule, benzonitrile *N*-oxide,[4] is reactive toward **1a** and **1b**; we report the complete characterization of the resultant cycloadducts and the reactivity of several other low-valent metal carbonyl complexes toward arylnitrile *N*-oxides.

Dichloromethane solutions of tetraethylammonium salts of **1a** and **1b** smoothly reacted with 1.3 mol equiv of benzhydroxamic acid chloride (mp 45–48 °C; **caution**: skin irritant)[5] upon warming from −78 to 0 °C in the presence of anhydrous K_2CO_3 to produce cycloadducts **2a** and **2b**, respectively. Complex **2b** was isolated as a tetraethylammonium salt (75% yield) by filtration and addition of excess diethyl ether at 0 °C. An analytical sample was obtained by recrystallization from $CH_3CN/(C_2H_5)_2O$ at −20 °C. Pure NEt_4^+ salt of complex **2a** could not be isolated due to product decomposition. Similarly K[18-crown-6]·**1a** and NEt_4^+·**1b** react with *m*-fluorobenzhydroxamic acid chloride to generate analytically pure cycloadducts K[18-crown-6]·**3a** and NEt_4^+ **3b**. Cycloadducts **2a**, **2b**, **3a**, and **3b** all display strong absorptions[6] in the 1670–1640-cm^{-1} region (exocyclic C=O) and medium to weak bands in the 1540–1520-cm^{-1} region (C=N).

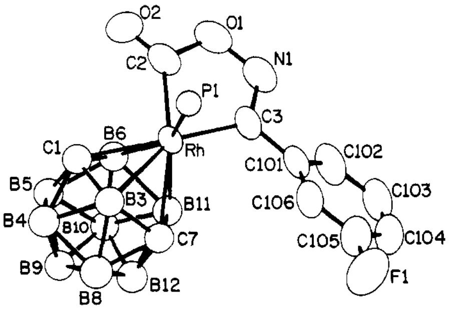
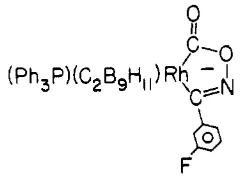


Figure 1.

An X-ray diffraction study was carried out on the $[PPN]^+$ salt of **3b**;[7] a projection of the anion is shown in Figure 1. Bond lengths within the metallacycle are not unusual for the valence bond representation shown in I, which can be described as a 4-rhodaisoxazolin-5-one.



I

The cycloadducts release carbon dioxide and benzonitrile or *m*-fluorobenzonitrile upon warming. When acetone solutions of the cycloadducts are maintained at 40 °C, the pale yellow of the metallacycle is replaced by a deep red. The 81.02-MHz $^{31}P\{^1H\}$ NMR spectrum of the red solution generated from **3a** showed $K[18\text{-crown-}6][3,3\text{-}(Ph_3P)_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ to be the only phosphorus-containing species present. The nature of the additional products has not been determined. Complexes **2b** and **3b** undergo similar thermal decomposition generating $[(C_2H_5)_4N][2,2\text{-}(Ph_3P)_2\text{-}2,1,7\text{-}RhC_2B_9H_{11}]$. When the decomposition reaction was performed at 40 °C under an atmosphere of CO, both **3a** and **3b** quantitatively regenerated **1a** and **1b**, respectively.

The 1,3-dipolar cycloaddition reaction of arylnitrile *N*-oxides could be extended to other low-valent metal-carbonyl complexes. Slow addition of an ether solution of benzonitrile *N*-oxide to a THF solution of $K[18\text{-crown-}6][Re(CO)_5]$[6] at −50 °C generates a white cycloadduct, **5a**,[6] analogous to **2a**. Complex **5a** is isolable (60–65%) as a remarkably stable salt, mp 155 °C dec. The IR spectrum of **5a** indicates that it has the expected metallacyclic structure analogous to **2a** or **2b**. The reaction of benzhydroxamic acid chloride with $K[18\text{-crown-}6][Mn(CO)_5]$[6] in the presence of anhydrous potassium carbonate at −20 °C produces the white cycloadduct **5b**.[6] IR and ^1H NMR spectroscopies indicate that **5b** is exactly analogous to **5a**; however, due to the low thermal stability of **5b**, satisfactory analytical data were not obtained.

Trimethylamine *N*-oxide has been commonly used to remove terminal carbonyl ligands (as CO_2), producing unsaturated and reactive metal centers.[8] For example, the complex $(\eta^5\text{-}C_5(CH_3)_5)Rh(CO)_2$ (**6**) has been converted to the dimeric complex $[(\eta^5\text{-}C_5(CH_3)_5)Rh(\mu\text{-}CO)]_2$ (**7**) by $(CH_3)_3NO$ in high yield.[9] Complex **6** reacts with *p*-chlorobenzonitrile *N*-oxide at −40 °C to produce yellow-white cycloadduct **8**. Infrared and ^1H NMR spectra indicate that **8** has the anticipated metallacycle structure.

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(1) (a) Hoffmann, R. *Angew. Chem.* **1982**, *94*, 725. See also Nobel Lecture, 1981. (b) Stone, F. G. A. *Acc. Chem. Res.* **1981**, *14*, 318 and references therein.

(2) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Wiley-Interscience: New York, 1972; p 684.

(3) Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.*, preceding communication in this issue.

(4) Huisgen, R. *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 565 and references therein.

(5) Werner, A.; Buss, H. *Ber. Dtsch. Chem. Ges.* **1894**, 2193.

(6) Supplementary material.

(7) Details will accompany the full report.

(8) Blumer, D. J.; Barnett, K. W.; Brown, T. L. *J. Organomet. Chem.* **1979**, *173*, 71–76 and references therein.

(9) Herrmann, W. A.; Bauer, C.; Plank, J.; Kalcher, W.; Speth, D.; Ziegler, M. L. *Angew. Chem., Int. Ed. Eng.* **1981**, *20*, 193.

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Complex **8**, thermally unstable (55 °C dec), slowly produces dimeric complex **7** in solution at 25 °C, a transformation that underscores the potential of this methodology for removing coordinated carbon monoxide ligands under exceedingly mild conditions.

Although this report apparently marks the first occasion that a nitrile oxide has been incorporated into a transition-metal complex, another class of 1,3-dipolar molecules, aryl and aroyl azides, were long ago reacted with Vaska's complex, *trans*-$(\mathrm{Ph_3P})_2(\mathrm{CO})\mathrm{IrCl}$, to produce one of the first dinitrogen complexes, *trans*-$(\mathrm{Ph_3P})_2(\mathrm{N_2})\mathrm{IrCl}$.[10] In light of our current findings, the mode of formation of this iridium–dinitrogen complex may involve 1,3-dipolar addition of the organic azide to the Ir–C(O) dipole in *trans*-$(\mathrm{Ph_3P})_2(\mathrm{CO})\mathrm{IrCl}$ to form the five-coordinate metallacycle $(\mathrm{Ph_3P})_2(\mathrm{Cl})\mathrm{ArC(O)}\overline{\mathrm{NN{=}NIrC}}(\mathrm{O})$, which subsequently decomposes to the observed products . The formation of the dinitrogen complex *trans*-$(\mathrm{Ph_3P})_2(\mathrm{N_2})\mathrm{IrCl}$ was originally proposed[10] to arise from a 1,3-oxidative addition of aroyl azide to the Ir center in *trans*-$(\mathrm{Ph_3P})_2(\mathrm{CO})\mathrm{IrCl}$ followed by reductive elimination of aroyl isocyanate to generate dinitrogen complex.

The structural characterization of cycloadduct **3b** demonstrates the first unequivocal 1,3-dipolar addition to a polarized M=C bond. Decomposition of the cycloadducts described here under mild conditions portends a powerful route to unsaturated, low-valent metal complexes and clusters. The utility of this chemistry lies in the exploitation of the unsaturated metal complexes formed by this means and probable application of nitrile oxide reactions to other metal–carbon and metal–metal bonded species. Work in this and related areas continues and will be reported at a later date.

Acknowledgment. We gratefully acknowledge financial support provided by the Office of Naval Research (Contract N00014-76-C-0390). We also thank the National Science Foundation for the purchase of the Syntex $P\bar{1}$ diffractometer and the Bruker WP-200 NMR spectrometer.

Supplementary Material Available: IR and NMR spectral and analytical data (1 page). Ordering information is given on any current masthead page.

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(10) Collman, J. P.; Kubota, M.; Vastine, F. D.; Sun, J. Y.; Kang, W. *J. Am. Chem. Soc.* **1968**, *90*, 5430 and references therein.

*Book Reviews**

Review of Textbooks for the "Brief" Organic Chemistry Course

(1) Introduction to Organic Chemistry. Third Edition. By D. Applequist (University of Illinois), C. H. DePuy (University of Colorado), and K. L. Rinehart (University of Illinois). John Wiley & Sons, New York, 1982. xiii + 343 pp. $22.92. (2) Organic Chemistry: A Brief Survey of Concepts and Applications. Second Edition. By P. S. Bailey, Jr., and C. A. Bailey (California Polytechnec State University). Allyn and Bacon, Inc., Boston, Mass. 1981 x + 418 pp. $20.95. (3) Introduction to Organic Chemistry. Third Edition. By W. H. Brown (Beloit College). Willard Grant Press, Boston, Mass. 1982. x + 493 pp. (4) A Short Course in Organic Chemistry. By E. E. Burgoyne (Arizona State University). McGraw-Hill Book Co., New York, NY. 1979. xii + 515 pp. $16.95. (5) The Essence of Organic Chemistry. By J. M. Cram and D. J. Cram (University of California—Los Angeles). Addition-Wesley Publishing Co., Reading, Mass. 1978. xv + 456 pp. $24.95. (6) Organic Chemistry: An Introduction. By J. E. Fernandez (University of South Florida). Prentice-Hall, Inc., Englewood Cliffs, NJ. 1982. xiv + 470 pp. $19.95. (7) Organic Chemistry: The Basis for Life. By B. Miller (University of Massachusetts). The Benjamin/Cummings Publishing Co., Inc., Menlo Park, CA. 1980. xv + 463 pp. $16.95. (8) Organic Chemistry. By J. D. Morrison (University of New Hampshire). Wadsworth Publishing Co., Belmont, CA. 1979. xii + 564 pp. $19.95. (9) Organic Chemisry: A Brief Contemporary Perspective. By C. W. Spangler (North Illinois University). Prentice-Hall, Inc., Englewood Cliffs, NJ. 1980. xv + 423 pp. $19.95.

The reviewer of textbooks designed for the "brief" organic chemistry course is faced with the same problems confronting the authors. The prefaces of these books reveal that there is no consensus as to the kind of students they should appeal to, nor is there agreement as to the extent or depth of coverage of the texts. Nevertheless, there does seem to be a consistency of style and content of all of these texts that make them relatively indistinguishable. Recognizing this, most instructors comtemplating a text adoption will consider only a few features as the basis for their decision. The true test, of course, is in the classroom. This reviewer has found, for example, that the Brown text has been effective for the past several years; but it is probable that any number of other texts would have served as well. As an aid to the instructor, five features (A–E) of the above texts have been examined, and those judged to be the most effective have been noted by a (+) in Table I.

Table I

	text feature analysis				
book no.	A	B	C	D	E
1	+		(+)	+	
2	+	+	+	+	+
3		+	+	+	+
4		+			
5	+			+	
6		+	+	+	
7					
8	+	+	+	+	+
9			(+)		+

A. Typography, Illustration, Etc. During the past decade authors and publishers have realized the pedagogical value of clear and attractive illustrations and typography. Effective use has been made of two-color, or contrasting shaded, high-lighted illustrations to emphasize important concepts, terms, structural features, reaction pathways, and mechanistic details. **B. Student Exercises.** The number and variety of problem exercises available to the student for review purposes appears adequate in all of these texts. Those noted in the table, however, were found to be either more thorough in their coverage or provided in-chapter review questions (some with answers and discussion) that were more likely to assure the students' mastery of the material. **C. Scope.** It is generally recognized that it is difficult to cover all of the material in the limited time normally available. It would appear that only the authors of the first text have attempted to limit the amount of material to what could reasonably be covered in one semester. The Spangler text is somewhat unusual in its organization being divided into "Core" and "Core Enrichment" sections. It is not clear in the absence of classroom testing how successful this approach might be. The other texts noted in the table provide an alternative means of coverage by placing special topics in supplementary sections or chapters. **D. Study Aids.** Most of the textbooks provide a separately published Student Study Guide, which gives the answers to the student exercises found in the text. The better of these also provides extensive discussions relating to study techniques and problem analysis. In this reviewer's opinion, the availability of a student study guide is a major factor in considering a text adoption. Since the Study Guides were not reviewed here, the table is more indicative of the presence of additional study aids such as glossaries, summaries of reaction types, and other review discussions. The Applequist text is the only one that includes an index of reactions not only according to functional groups but also arranged by expected organic products. **E. Spectroscopy.** With the increasing importance of spectroscopy to organic chemistry, it is surprising that most of the texts do not include more than a brief discussion. Only the Brown texts attempt to incorporate an optional dis-

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* Unsigned book reviews are by the Book Review Editor.