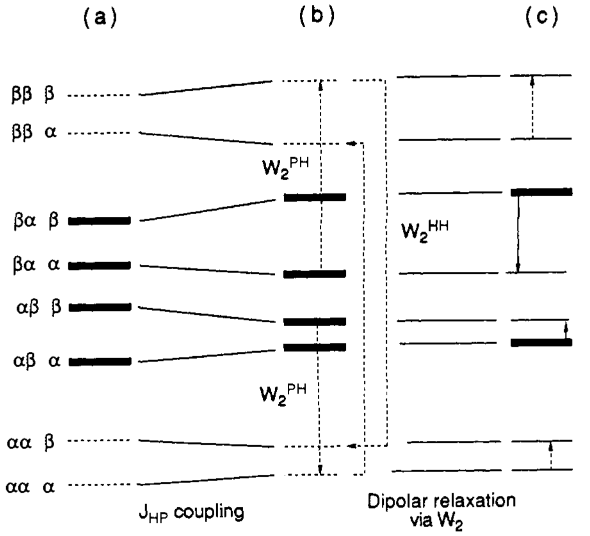

Figure 3. Energy levels for the HH'P (AMX) spin system with individual spin designations in the order of $H_{trans}H_{cis}P$. Energies are not to scale. (a) No ^{31}P–^{1}H coupling. Only the ^{1}H $\alpha\beta$ and $\beta\alpha$ levels are overpopulated from para H_2 addition, with underpopulations indicated by dotted lines. (b) After introduction of couplings with J_{PH}trans > 0 and J_{PH}cis < 0, dipolar relaxation occurs between levels connected by dotted lines. (c) Populations after dipolar relaxation with enhanced transitions shown as solid arrows.

more pronounced effect being observed in the resonance for the phosphorus trans to one of the hydrides. All examples show an E/A phase, a peak separation of $^{2}J_{PH}$trans + $^{2}J_{PH}$cis, and an estimated signal enhancement of 6–10-fold. Coincidentally, the spectrum generated by using para H_2 (Figure 2, trace (a)) can be duplicated with the ^{1}H–^{31}P INEPT pulse sequence.[3] This is shown as trace (c) in Figure 2. In INEPT the hydride ^{1}H populations are selectively inverted, and these population differences are transferred onto the ^{31}P transitions. In the present study, the ^{1}H populations are perturbed chemically, with the population differences transferred to ^{31}P by dipolar relaxation.

The observed polarization in the resonance of P trans to H can be understood in terms of the energy level diagrams of Figure 3 for the HH'P (AMX) spin system with individual level spin functions designated in the order $H_{trans}H_{cis}P$. In Figure 3a only the ^{1}H $\alpha\beta$ and $\beta\alpha$ levels are overpopulated as a result of the oxidative addition reaction using para H_2. Upon introduction of coupling with J_{PH}trans > 0 and J_{PH}cis < 0, the level ordering is modified to that of Figure 3b. Since dipolar relaxation via two-quantum transitions (W_2) is distance dependent, it occurs preferentially through cis partners as shown by the dotted lines on Figure 3b for H_{cis}–P and H–H leading to the population modifications shown in 3c. Only two levels, $\alpha\beta$ α and $\beta\alpha$ β, remain unaffected and, by virtue of para H_2 addition, overpopulated. The ^{31}P NMR transitions in enhancement are shown in 3c by the solid arrows, while those which are absent are indicated by dotted arrows.

The above results thus demonstrate that spin overpopulations generated by oxidative addition of para H_2 can be transferred effectively to ^{31}P nuclei resulting in NMR signal enhancement and polarization. Other systems including Vaska's complex, $IrCl(CO)(PPh_3)_2$, show similar results regarding polarization transfer in H_2 addition products, and initial investigations have yielded polarization transfer to ^{13}C nuclei in ^{13}C NMR spectra of hydrogenation products.[9] Because potential population inversions using para H_2 are larger than are obtainable through pulse sequences, we think this procedure, where appropriate, will prove valuable for signal enhancement and spectroscopic analysis.

Acknowledgment. We thank the National Science Foundation (CHE 86-05033 and CHE 89-09060) for support of this work and the Johnson Matthey Co., Inc. for a generous loan of iridium salts.

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[9] Eisenschmid, T. C.; Eisenberg, R. Results to be published.

The Generation of 2-Vinylcyclopentene-1,3-diones via a Five-Component Coupling in the Coordination Sphere of Chromium

Yao-Chang Xu, Cynthia A. Challener,[1] Vera Dragisich,
Timothy A. Brandvold, Glen A. Peterson, and
William D. Wulff*

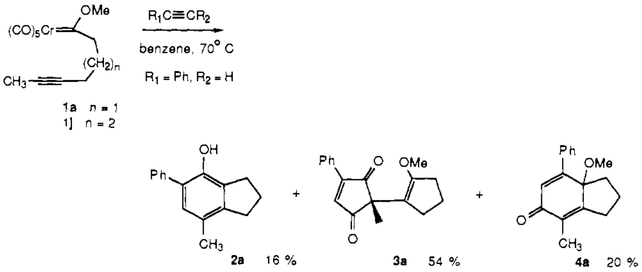
Searle Chemistry Laboratory, Department of
Chemistry, The University of Chicago
Chicago, Illinois 60637

Paul G. Williard

Brown University, Department of Chemistry
Providence, Rhode Island 02912

Received April 7, 1989

The chemistry of Fischer carbene complexes and alkynes is extremely fertile and is known to produce 4-alkoxyphenols, phenols, furans, cyclopentadienes, cyclobutenones, vinylketenes, cyclohexadienones, 1,3-dienes, pyrones, and cyclopentenones.[2-4] A year ago we communicated the first examples of the intramolecular reactions of alkyne carbene complexes of the type **1** involving the annulation of the carbene complex **1** with a number of alkynes.[5,6] In the case of phenylacetylene, the only product that could be isolated from the reaction in acetonitrile was the two-alkyne phenol **2a** in 52% yield.



The reactions of carbene complexes with acetylenes are known to be sensitive to solvent,[2c,7] and the reaction of **1a** with phenylacetylene proved to be no exception. The reaction of **1a** with phenylacetylene in nonpolar, noncoordinating solvents such as benzene produces two new structural types, the 2-vinylcyclopentene-1,3-dione **3a** and the cyclohexa-2,5-dienone **4a**, both of which are unprecedented from the reaction of carbene complexes and acetylenes. Final assignment of the structure of **3a** was made by X-ray diffraction.[8] Pyrones having one alkyne and two carbon monoxides[9] and phenols having two alkynes and one carbon monoxide[9b,10] have both been observed, but there has never been

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[1] National Institute of Health Predoctoral Fellow.

[2] Reviews: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL., 1984. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. (d) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.; Greenwich, CT, 1989; Vol. 1.

[3] For recent citations, see: Wulff, W. D.; McCallum, J. S.; Kunng, F. A. *J. Am. Chem. Soc.* **1988**, *110*, 7419.

[4] Cyclopentenones: (a) Herndon, J. W.; Turner, S. U.; Schnatter, W. F. K. *J. Am. Chem. Soc.* **1988**, *110*, 3334. (b) Challener, C. A.; Kim, O. K.; Murray, C. K.; Wulff, W. D., submitted for publication.

[5] Wulff, W. D.; Xu, Y. C. *Tetrahedron Lett.* **1988**, *29*, 415.

[6] For an intramolecular enyne reaction, see: Korkowski, P. F.; Hoye, T. R.; Rydberg, D. R. *J. Am. Chem. Soc.* **1988**, *110*, 2676.

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[8] (a) See Supplementary Material. (b) NOE experiments reveal that **3k** has the Z configuration.[8a]

[9] (a) Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *J. Am. Chem. Soc.* **1984**, *106*, 5363. (b) Semmelhack, M. F.; Park, J. *Organometallics* **1986**, *5*, 2550.

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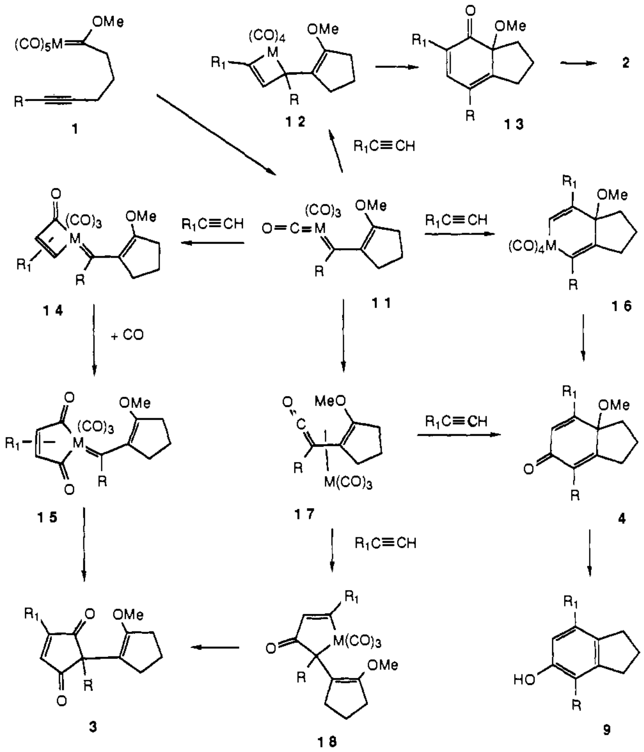
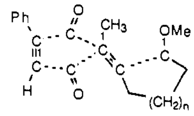
Scheme I



a product obtained from the reactions of carbene complexes and alkynes which resulted from the incorporation of two alkynes and two carbon monoxides in addition to the carbene ligand. The assembly of pieces is thus illustrated by the construction **5**. We have observed these cyclopentenediones in intermolecular reactions on only two occasions as minor products in the reactions of complexes **6k** and **6l** with 1-pentyne in hexane as solvent.



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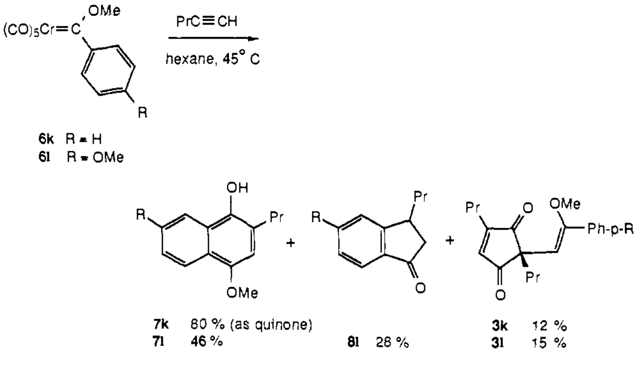
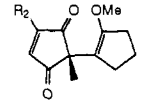
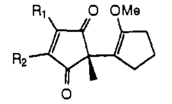
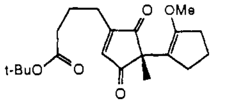
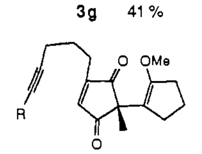
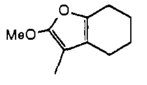
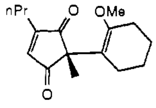
For reasons that we do not yet understand the formation of the cyclopentenedione product is greatly favored in intramolecular reactions. As indicated by the examples in Table I, the very easily



prepared carbene complex **1**[10e] and simple functionalized acetylenes can be used to directly access highly functionalized bicyclopentanoids in a single transformation that is of only moderate overall yield but which occurs with the formation of six new carbon–carbon bonds! With this level of complexity these reactions should be attractive for the preparation of advanced synthetic intermediates. This reaction can also be used to generate the cyclohexenylcyclopentenedione **3j** from the homologated complex **1j**, but the yield is slightly lower and is accompanied by the formation of the furan **22** which may arise via a mechanism that has been previously discussed.[3,9b,11]

Table I. Vinylcyclopentenediones from Chromium Carbene Complex **1**[a]

entry	alkyne		Minor Products	Cyclopentendione	
	R$_1$	R$_2$	Yield	Yield	
					
a	H	Ph	**2a** (16 %), **4a** (20 %)	**3a**	54 %
b	H	*n*-Pr	**2b** (18 %), **9b** (15%)	**3b**	55
c	H	CH$_3$	**2c** (6 %), **4c** (3 %), **9c** (2 %)	**3c**	54
d	H	Me$_3$Si	**2d** (8 %)	**3d**	46
					
e	Et	Et	**4e** (11 %)	**3e**	27 %
f	H	H	**2f** (9 %), **9f** (10 %), **4f** (8 %)	**3f**	34 %
					
g	H	(CH$_2$)$_3$CO$_2{}^t$Bu	**2g**,[b] **9g**,[c] **13g**[b]	**3g**	41 %
					
h i	H	(CH$_2$)$_3$CCR		**3h** **3i**	R = SiMe$_3$ 39 % R = H 36
					
j[d]	H	*n*-Pr	**13j** 9 % **22** 30 %	**3j**	37 %

[a] Unless specified, all reactions were carried out in benzene under an argon atmosphere at 5 mM in complex **1a** with 3 equiv of alkyne at 70 °C for 12–24 h. [b] Detected by ^{1}H NMR. [c] Yield not determined. [d] Reaction with complex **1b**.

A consideration of possible mechanisms for the formation of these cyclopentene-1,3-diones leads to the identification of the two interesting possibilities indicated in Scheme I. One intriguing possibility involves the addition of an alkyne to the carbon–metal bond of a carbon monoxide ligand to the intermediate vinylcarbene complex **11**.[12] The resultant metallacyclobutenone **14**[13] then could undergo a carbon monoxide insertion to give the maloyl complex **15**. The final conversion of **15** to the cyclopentenedione **3** would be reminiscent of the coupling of maloyl and vinylidene ligands that has been recently proposed by Liebeskind for the formation of methylenecyclopentene-1,3-diones.[14] Another possibility involves the reductive coupling of the alkyne with the carbon–carbon bond of the coordinated ketene in the vinyl ketene complex **17** to give **18** which upon CO insertion and reductive elimination would generate **3**. Further studies will be needed before a distinction between these possible mechanisms can be made.

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(13) Chetcuti, M. J.; Green, K. A. *Organometallics* **1988**, *7*, 2450.

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The formation of the cyclohexadienone **4a** is the result of an unprecedented "para"-two-alkyne annulation. Reduction of **4a** with zinc and acetic acid gave the phenol **9a** which was found not to be identical with the phenol **2a** also isolated from this reaction. Although phenol products resulting from the incorporation of two molecules of alkyne, a carbon monoxide and a carbene ligand, have been observed before, they have only been reported with the regiochemistry indicated by **2** in which the carbene and carbon monoxide ligands are introduced in adjacent positions in the newly formed aromatic nuclei.[10] The "para"-two-alkyne phenol (and dienone) products were observed for the reactions in entries a, b, c and f in Table I. The assignment of their structures was made for the phenols **2b** and **9b** on the basis of NOE experiments and ^{13}C labeling experiments which are discussed in the Supplementary Material. Possible mechanisms to account for the formation of para-two-alkyne phenols include a [4 + 2] cycloaddition of an alkyne to the vinylcarbene complex intermediate **11** and a [4 + 2] cycloaddition to the vinylketene complexed intermediate **17**. Current studies are directed to determine how the reaction conditions can lead to differentiation between "para"- and "ortho"-two-alkyne annulated products.

The uniqueness of the transformations leading to the 2-vinylcyclopentene-1,3-diones and para-two-alkyne phenols should promote further study of the mechanistic issues and synthetic opportunities raised by these initial observations.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-8517103) awarded to W.D.W. and by a grant from the National Institutes of Health (CA 01330) awarded to P.G.W. The National Institute of Health has provided a predoctoral training grant for C.A.C. (No. GM 07183). Some of the mass spectral data were obtained at the Midwest Center for Mass Spectrometry and NSF Regional Instrument Facility (CHE-8211164). The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program and by the NCI via the University of Chicago Cancer Research Center (CA-14599).

Supplementary Material Available: Spectral data for all new compounds, structural assignment of the phenols **2** and **9**, and X-ray diffraction data for compound **3a** (21 pages). Ordering information is given on any current masthead page.

Combining Spontaneous Molecular Assembly with Microfabrication to Pattern Surfaces: Selective Binding of Isonitriles to Platinum Microwires and Characterization by Electrochemistry and Surface Spectroscopy

James J. Hickman, Chaofeng Zou, David Ofer,
Pierre D. Harvey, and Mark S. Wrighton*

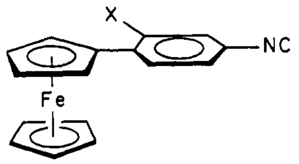
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Paul E. Laibinis, Colin D. Bain, and George M. Whitesides*

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received May 1, 1989

We wish to report selective modification of the Pt microelectrodes of a microfabricated array by using redox reagents I and II having an isonitrile, –NC, functional group, Scheme I. Building on studies of macroscopic surface chemistry,[1] selective coordination chemistry of RSH and RCOOH has been recently used to assemble monolayers of long chain hydrocarbons or perfluorocarbons onto mixed-metal microwire arrays.[2] Our new results demonstrate the ability to combine microfabrication and surface coordination chemistry to pattern a surface with *redox active molecular reagents*.



I, X = H;
II, X = Cl.

The rationale for investigating the binding of RNC reagents to Pt is that RNC is isoelectronic with CO which is known to bind firmly to Pt.[3] It has already been shown that gas-phase CH$_3$NC will bind to (111) Pt[4] and (111) Rh[5] in the manner implied in Scheme I. A large number of RNC transition metal complexes are known,[6] and these can be viewed as derivatives of CO complexes. Importantly, RNC ligands offer considerable diversity in properties via variation in R.[7] While a few functional groups, e.g., –SH or olefin, have been used to bind redox reagents to electrode surfaces,[1a,d,e] the use of the –NC group for surface attachment has not been explored.

Electrochemical and surface spectroscopic techniques have been used to establish the binding of I and II to Pt electrode surfaces. I and II were prepared from the corresponding ferrocenylanilines[8] and incorporate the reversible redox function (the ferrocenyl group) and unique elements (e.g., Fe in I or Cl in II) to facilitate surface analysis by X-ray photoelectron spectroscopy, XPS,[8] or Auger electron spectroscopy, AES.[8] Typically, pretreated Pt[9] was exposed to ~1 mM I or II in CH$_3$CN solvent for 5 min at 298 K under Ar, removed, and washed thoroughly with CH$_3$CN, prior to analysis. XPS shows the Fe 2p$_{3/2}$, 707.9 eV, and N 1s signals, 398 eV, at intensities consistent with about one monolayer of intact RNC. The same modification and analysis procedure using phenylferrocene, containing no –NC group, shows no surface-confined Fe-containing material. Fourier transform infrared spectroscopy, FTIR, shows the –NC vibration at 2137 cm^{-1} for I bound to Pt[10] vs 2127 cm^{-1} for I in CH$_2$Cl$_2$. For comparison,

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* Address correspondence to this author.

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(8) Experimental details concerning synthesis, XPS, and AES are given in the Supplementary Material.

(9) Commercial Pt, vacuum deposited Pt, or microelectrodes were sonicated for ~30 min in each of the three solvents of increasing polarity (usually hexane, CH$_2$Cl$_2$, and CH$_3$OH) followed by an O$_2$ plasma treatment in a Harrick PDC-23G for 1-5 min, 0.3 Torr at medium power (40 W), and used immediately.

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