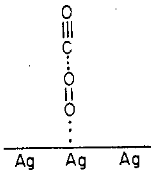
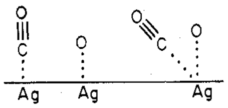
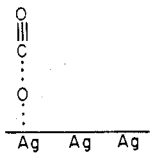
Scheme II



Scheme III



Scheme IV



species active in oxidation, one would envisage corresponding Schemes III and IV.

From our matrix warm-up experiments $(OC)Ag^+,O_2^-$ appears to be a very unstable compound which certainly decomposes at temperatures exceeding 40 K. It would therefore appear exceedingly unlikely that a related surface complex could have anything other than a very transient existence on a silver catalyst in the working temperature range of 100 °C. However, such a species could be a short-lived precursor to the CO_3 surface intermediate which is supposed to be formed from the CO and preadsorbed oxygen on silver and which is thought to be responsible for $^{16}O/^{18}O$ isotopic exchange processes between $^{12}C^{16}O$ and $^{18}O_2$.[7]

In our $Ag/O_2/CO$ matrix experiments, only *very small* quantities of CO_2 were detected on deposition, indicating that oxidation reactions on the hot silver source, in the gas phase or in the matrix, were insignificant. Of greater importance is the fact that CO_2 generation was not observed on warming $(OC)Ag^+,O_2^-$ to 40 K at which temperature the complex was undergoing some kind of decomposition. Furthermore, evidence for a $Ag-CO_3$ or $Ag-CO_2$ reaction intermediate was not observed at any time during the matrix decomposition of $(OC)Ag^+,O_2^-$.

Conclusion

One may conclude that although $(OC)Ag^+,O_2^-$ does not act as a precursor for CO_2 under cryogenic conditions, it may nevertheless be a suitable localized bonding model for CO/O_2 surface complexes. It certainly displays all of the properties anticipated for CO coordinated to an oxidized silver atom even though it does not simulate the actual oxidation process to CO_2. This may be the result of a kinetic impediment to OO bond rupture at the low temperatures employed. Alternatively, the $O_2^-{}_{ads}$ species may not be active in CO oxidation, in which case a complex such as $[(OC)Ag]^+O^-$ would be a more appropriate synthetic goal. In the event that the Eley–Rideal type of mechanism is a better description of the surface oxidation process, then modeling the CO/O_2 oxidation on a silver atom may prove to be impossible.

Acknowledgment. We thank the National Research Council of Canada for financial support.

Registry No. $(OC)Ag(O_2)$, 60594-86-7; $[Ag(CO)]^+$, 60594-87-8.

References and Notes

(1) D. McIntosh and G. A. Ozin, *Inorg. Chem.*, preceding paper in this issue.
(2) R. Ugo, *Catal. Rev.*, **11**, 225 (1975).
(3) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975).
(4) W. M. H. Sachtler, *Catal. Rev.*, **4**, 27 (1970), J. H. Lunsford, *ibid.*, **8**, 135 (1975).
(5) P. A. Kilty and W. M. H. Sachtler, *Catal. Rev.*, **10**, 1 (1974).
(6) H. H. Voge and C. R. Adams, *Adv. Catal.*, **17**, 151 (1967); R. B. Clarkson and A. C. Cirillo, Jr., *J. Catal.*, **33**, 392 (1974).
(7) G. W. Keulks and J. F. Outlaw, Jr., "Proceedings of the Fifth International Conference on Catalysis", 1973, J. W. Hightower, Ed., North-Holland Publishing Co., Amsterdam, 1973, paper 65, p 945.
(8) P. Kündig, M. Moskovits, and G. A. Ozin, *J. Mol. Struct.*, **14**, 137 (1972).
(9) M. Moskovits and G. A. Ozin, *J. Appl. Spectrosc.*, **26**, 487 (1972).
(10) E. P. Kündig, M. Moskovits and G. A. Ozin, *Angew. Chem., Int. Ed. Engl.*, **14**, 292 (1975); M. Moskovits and G. A. Ozin in "Cryochemistry", Wiley, New York, N.Y., 1976, Chapter 9.
(11) D. McIntosh and G. A. Ozin, *J. Am. Chem. Soc.*, **98**, 3167 (1976).
(12) H. Huber, E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Am. Chem. Soc.*, **97**, 2097 (1975).
(13) D. McIntosh and G. A. Ozin, *Inorg. Chem.*, **16**, 51 (1977).
(14) H. J. Guirand and C. S. Foote, *J. Am. Chem. Soc.*, **98**, 1984 (1976); J. Rolfe, *J. Chem. Phys.*, **40**, 1664 (1964).
(15) C. W. Dekock and D. A. Van Liersburg, *J. Am. Chem. Soc.*, **94**, 3235 (1972); *J. Phys. Chem.*, **78**, 134 (1974).
(16) Y. Souma, J. Iyoda, and H. Sano, *Inorg. Chem.*, **15**, 968 (1976).
(17) P. Politzer and S. D. Kasten, *Surf. Sci.*, **36**, 186 (1973).
(18) J. Pritchard and M. L. Sims, *Trans. Faraday Soc.*, **59**, 437 (1963).
(19) W. Klotzbücher and G. A. Ozin, *J. Am. Chem. Soc.*, **97**, 3965 (1975).
(20) W. Klotzbücher and G. A. Ozin, *J. Am. Chem. Soc.*, **97**, 2672 (1975).
(21) H. Huber, W. Klotzbücher, A. Vander Voet, and G. A. Ozin, *Can. J. Chem.*, **51**, 2722 (1973).
(22) E. L. Force and A. T. Bell, *J. Catal.*, **40**, 356 (1975).

Contribution from the Department of Chemistry,
University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

Metal Carbonyl Induced Reactions of Azirines. Coupling and Insertion by Diiron Enneacarbonyl

HOWARD ALPER* and JOHN E. PRICKETT

Received April 20, 1976 AIC604916

Azirines undergo coupling and insertion reactions with diiron enneacarbonyl in benzene to give pyrroles, ketones, ureadiiron hexacarbonyl complexes, and diimine complexes. Substituent effects have a significant influence on the course of the reaction. A mechanism is proposed which involves carbon–nitrogen bond cleavage of the azirine ring. Treatment of 1-azidostyrene with $Fe_2(CO)_9$ results in the formation of some of the same products as obtained using azirines as the substrates.

The chemistry of azirines has been a subject of great interest in recent years. Splendid work by Hassner,[1a] Padwa,[1b,c] Schmid,[1d] and others has resulted in new synthetic routes to heterocycles via cycloaddition to the ring-opened azirine. In addition, metal carbonyls can effect fascinating ring-cleavage reactions of small ring systems [e.g., vinyloxiranes,[2a] vinylcyclopropanes[2b]] to give interesting organic or organometallic products.

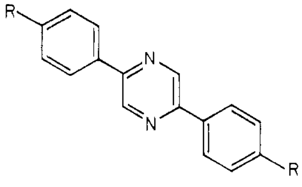
On the basis of these results, it seemed conceivable that metal carbonyls might induce azirines to form novel organometallic complexes and/or to provide simple and convenient synthetic approaches to heterocyclic systems. The

Table I. Yields, Melting Points, and Analytical Data for Complexes Obtained from Reactions of Azirines with $Fe_2(CO)_9$

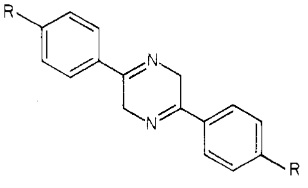
				% found (calcd)			
Azirine	Products	Yield,[a] %	Mp, °C	C	H	N	Fe
4a	**5a**	7.8	90–92	51.82 (51.40)	3.11 (2.74)	5.04 (5.45)	21.66 (21.73)
	6a	1.0	101–103	51.41 (50.96)	2.74 (2.60)	5.44 (5.17)	20.73 (20.60)
	7a	3.0	134–136	51.72 (51.15)	2.41 (2.24)	5.04 (5.19)	21.16 (20.68)
	8a	12.8	142–144[b]				
	9a	1.0		72.88 (72.67)	4.09 (4.53)		10.02 (9.65)
	10a	0.5					
4b	**5b**	4.5	96–99	53.23 (53.37)	3.27 (3.37)	4.80 (5.18)	20.06 (20.62)
	6b	<1	124–126	52.28 (52.67)	3.56 (3.18)	4.86 (4.91)	19.81 (19.59)
	7b	2.0[c]	157–160	52.18 (52.85)	3.06 (2.84)	4.56 (4.93)	19.11 (19.66)
	8b	19.7	196–198[d]				
	9b	1.0					
4c	**5c**	2.4		40.17 (39.53)	2.09 (1.80)	4.20 (4.17)	16.30 (16.62)[e]
	6c	0.9	153–154				
	7c	4.5		39.77 (39.59)	1.31 (1.44)	4.09 (4.01)	16.42 (16.00)
	8c	16.5	213–215	50.82 (50.96)	2.94 (2.94)[f]		
	10c	0.2					
4d	**6d**	9.1	126–127	53.00 (52.67)	3.49 (3.18)	5.13 (4.91)	19.23 (19.59)
	8d	5.2	133–134[g]				
	10d	4.8					
4e	**5e**	1.5	104–106				
	6e	9.0	120–122	54.28 (54.21)	4.18 (3.71)	4.75 (4.68)	18.58 (18.67)
	10e	2.0					
4f	**6f**	17.6	82.5–83.5	45.83 (45.45)	4.43 (4.42)	6.00 (5.58)	22.47 (22.24)
	10f	3.6					
4g	**6g**	18.8	138 dec	54.00 (54.21)	3.48 (3.71)	5.06 (4.68)	18.55 (18.67)
	10g	5.2					

[a] Yields are of analytically pure products. Crude yields were much higher. [b] Literature mp 143–144 °C [G. A. Kreutzberger and P. A. Kalter, *J. Org. Chem.*, **25**, 554 (1960)]. [c] Molecular weight by osmometry ($CHCl_3$) 554 (calcd 568). [d] Literature mp 197 °C [R. Holleman, *Recl. Trav. Chim. Pays-Bas*, 6, 73 (1887)]. [e] Bromine: calcd, 23.80%; found, 24.08%. [f] Bromine: calcd, 42.12%; found, 42.49%. [g] Literature[9] mp 136 °C.

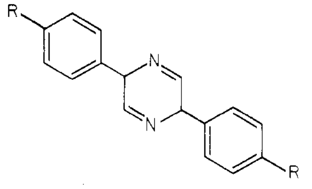
latter possibility has been demonstrated by the reported dimerization, using group 6 metal carbonyls, of 2-arylazirines to pyrazines (**1**) and isomeric diaryl-3,6-dihydropyrazines (**2**, **3**) under mild conditions.[3] It was of considerable interest to learn the effect, if any, of the metal carbonyl on the course of the reaction. This paper describes different and interesting reactions of diiron enneacarbonyl [$Fe_2(CO)_9$] with a variety of azirines.[4]



1



2



3

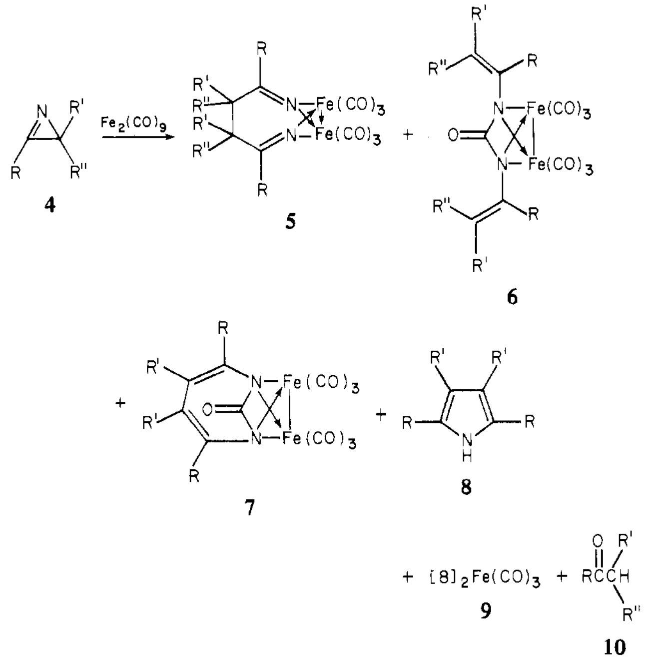
R = H, CH_3, OCH_3

Results and Discussion

A series of 2-aryl (**4a–c**) and 2,3-di- or trisubstituted azirines (**4d–g**) were reacted with $Fe_2(CO)_9$ in dry benzene at 50 °C for 3–4 h. Some or all of the air-stable organometallic and organic products, **5–10** (Scheme I), were isolated from these reactions. Yields and analytical data for **5–10** are listed in Table I. The structures of the products were elucidated on the basis of analytical and spectral data (Table II).

The infrared (ir) terminal metal–carbonyl stretching bands for the diiron hexacarbonyl complex **5** occur at frequencies similar to those reported for the related phthalazine[5] and diazepine[6] complexes. The nuclear magnetic resonance (NMR) spectra of **5** [R′ = R″ = H] were characterized by a signal for the methylene protons in the region of δ 2.50, while the mass spectra displayed molecular ion peaks, followed by successive loss of six carbonyl groups.

Scheme I



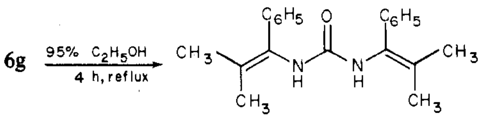
a, R = C_6H_5, R′ = R″ = H
b, R = p-$CH_3C_6H_4$, R′ = R″ = H
c, R = p-BrC_6H_4, R′ = R″ = H
d, R = C_6H_5, R′ = CH_3, R″ = H
e, R = C_6H_5, R′ = C_2H_5, R″ = H
f, R = CH_3, R′ = $CH(CH_3)_2$, R″ = H
g, R = C_6H_5, R′ = R″ = CH_3

Table II. Pertinent Ir, NMR, and Mass Spectra for 4-$Fe_2(CO)_9$ Reaction Products

Product	Ir,[a] cm^{-1} $\nu_{C\equiv O}$	Ir,[a] cm^{-1} $\nu_{C=O}$	NMR δ,[b] ppm	m/e
5a	2070, 2030, 1995, 1975, 1960 sh		2.50 (4 H), 6.95–7.55 (10 H)	514, 486, 458, 430 402, 374, 346
5b	2070, 2030, 1994, 1950 sh		2.35 (6 H), 2.65 (4 H), 6.75–7.30 (8 H)	542, 514, 486, 458, 430, 402, 374
5c	2070, 2028, 1995, 1973, 1963 sh		2.45 (4 H), 6.75–7.65 (8 H)	672, 644, 616, 588, 560, 532, 504
5e	2075, 2033, 1990, 1977, 1950			570, 542, 514, 486, 458, 430, 402
6a	2082, 2040, 2000	1730	5.15 (4 H), 6.95–8.00 (12 H)	514, 486, 458, 430, 402, 374, 346[c]
6b	2080, 2040, 1990	1733	2.40 (6 H), 5.20 (4 H), 7.10–8.00 (8 H)	570, 542, 514, 486, 458, 430, 402, 374
6c	2085, 2040, 1995	1735	5.18 (4 H), 7.10–8.10 (10 H)	
6d	2080, 2040, 2001	1730	1.55 (6 H), 5.55 (2 H), 7.30 (10 H)	570, 542, 514, 486, 458, 430, 402, 374
6e	2080, 2040, 1995	1735	0.92 (6 H), 1.87 (4 H), 5.45 (2 H), 7.20–7.50 (10 H)	598, 570, 542, 514, 486, 458, 430, 402
6f	2080, 2040, 2000	1736	0.91 (12 H), 1.88 (6 H), 2.47 (2 H), 4.90 (2 H)	502, 474, 446, 418, 390, 362, 334, 306
6g	2080, 2039, 1998	1732	1.51 (6 H), 1.78 (6 H), 7.30 (10 H)	598, 570, 542, 514, 486, 458, 430, 402
7a	2078, 2040, 2005, 1988	1725	6.70–7.60 (12 H)	540, 512, 484, 456, 428, 400, 372, 344
7b	2080, 2045, 2000, 1990	1728	2.41 (6 H), 6.85–7.60 (10 H)	568, 540, 512, 484, 456, 428, 400, 372
7c	2078, 2045, 2005, 1990 sh	1730	6.70–7.90 (10 H)	698, 670, 642, 614, 586, 558, 530, 502
8a			6.55 (2 H), 7.40 (10 H), 8.40 (1 H)	219
8b			2.33 (6 H), 6.55 (2 H), 7.20–7.50 (8 H), 8.70 (1 H)	247
8c			6.55 (2 H), 7.20–7.50 (8 H), 8.60 (1 H)	377
8d[d]			2.23 (6 H), 7.20–7.70 (10 H), 8.00 (1 H)	247
9a	2034, 1982		6.50 (4 H), 6.90–7.70 (20 H), 8.10 (2 H)	578, 550, 522, 494, 219
9b	2030, 1982		2.37 (12 H), 6.5 (4 H), 7.10–8.10 (16 H), 8.40 (2 H)	634, 606, 578, 550
10a		1690	2.59 (3 H), 7.2–8.1 (5 H)	120
10c		1676	2.60 (3 H), 7.60 (2 H), 7.88 (2 H)	199
10d		1685	1.18 (3 H), 2.95 (2 H), 7.2–8.1 (5 H)	
10e		1681	1.03 (3 H), 1.75 (2 H), 2.90 (2 H), 7.3–8.0 (5 H)	148
10f		1705	0.90 (7 H), 2.12 (3 H), 2.25 (2 H)	
10g		1680	1.20 (6 H), 3.45 (1 H), 7.3–8.1 (5 H)	

[a] $CHCl_3$ solution; the relative intensities of the listed bands are all *strong*. [b] $CDCl_3$ solution with $(CH_3)_4Si$ as internal standard. [c] Molecular ion peak not observed. [d] λ_{max} (95% ethanol) 208, 321 nm.

The positions of the terminal metal and urea carbonyl ir bands for complexes **6** and **7** were very close to those for urea complexes formed by the reaction of nitro compounds with $Fe_2(CO)_9$.[7] The urea carbonyl absorption occurs at a significantly lower frequency than that for a carbonyl bridging two iron atoms.[5,8] Vinyl proton signals occurred at δ 4.90–5.55 in the NMR of **6** [except **6g**], but not **7**, and olefinic methyl absorptions appeared in appropriate cases for **6**. The molecular ion peaks for **7** occurred at two m/e units less than that for the corresponding complex **6**, but successive loss of seven carbonyl groups was observed in the mass spectra of both series of complexes. When **6g** was refluxed in 95% ethanol, the divinylurea **11** was obtained in 83% yield.



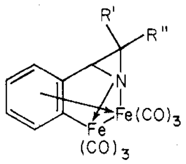
11

The pyrroles formed in the $Fe_2(CO)_9$ reactions are known compounds (except **8c**) and were identified by comparison of melting points and spectral results with literature data. It is noteworthy that only 3,4-dimethyl-2,5-diphenylpyrrole (**8d**),[9] but no isomeric pyrroles, was isolated using 2-phenyl-3-methylazirine (**4d**) as the reactant.

The bis(pyrrole)iron tricarbonyl, **9**, which was formed in several instances, exhibited ir carbonyl stretching bands characteristic of an $L_2Fe(CO)_3$ complex.[10] The mass spectrum of **9** showed a pyrrole radical ion fragment, in addition to the molecular ion peak and peaks resulting from successive loss of three carbonyls. The NMR spectrum of **9** was similar to that of the free pyrrole ligand.

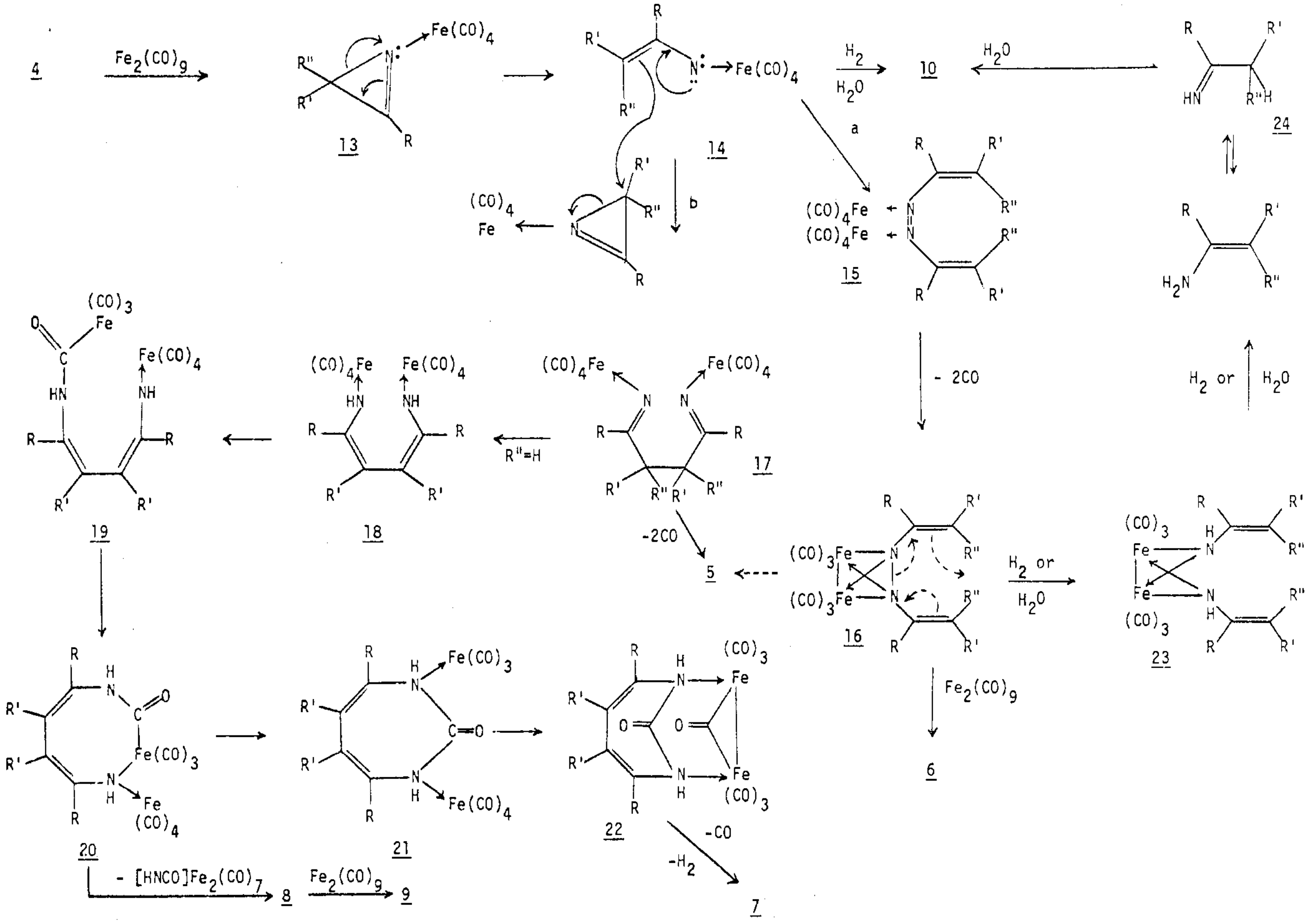
Ketones (**10**) were isolated from some of the reactions and were identified by comparison of spectral properties with those of authentic materials.

Ortho-metalated complexes[11] of structural type **12**, analogous to those derived from Schiff bases[12] or thiones,[13] were not formed from azirines having an aryl group at the 2 position. It is likely that complex **12** would be a fairly strained system and could only form if the nitrogen lone pair is properly



12

Scheme II



oriented with respect to the iron attached to the ortho position of the benzene ring.

It is significant that no free or complexed pyrazines or dihydropyrazines were isolated in any of these reactions suggesting different reaction pathways for the iron and group 6 metal carbonyls. The formation of **5**–**10** can be rationalized on the basis of carbon–nitrogen rather than carbon–carbon [$M(CO)_6$] bond cleavage of the reactant heterocycle.

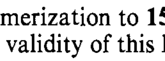
The initial step in the azirine–$Fe_2(CO)_9$ reactions is probably n-donor complexation (**13**) followed by carbon–nitrogen bond cleavage to give the nitrene complex **14** [Scheme II]. Conversion of **14** to the diiron hexacarbonyl complex 5 can occur via routes a and/or b: (a) dimerization to the azo complex **15**, followed by loss of two carbonyl groups with concurrent metal–metal bond formation (**16**), and subsequent Cope rearrangement; (b) addition to the azirine complex **13** to give **17** which can then afford **5** [similar to **15** → **16**]. Insertion of carbon monoxide into the N–N bond of **16** would give the urea complex **6**.

Compounds **7**–**9** may be formed via complex **20**, generated by tautomerization of **17** to **18**, ligand migration (**19**), and then cyclization. Collapse of **20** would give the pyrrole **8** and the iron tricarbonyl complex **9** [with more $Fe_2(CO)_9$]. Rearrangement of **20** to **21** followed by Fe–Fe bond formation (**22**) and loss of carbon monoxide and hydrogen would generate the urea complex **7**.

Complex **16** may serve as the ketone (**10**) source as well. Cleavage of the N–N bond of **16** by hydrogen (from **22** → **7** and/or from solvent) or H_2O (during workup) would afford **23** which is convertible to the enamine **24** on further hydrogen abstraction. The ketone **10** would result on subsequent hydrolysis of **24**. It is conceivable that **10** could be formed via hydrogen abstraction by **14**.

Significant variations in product distribution were observed in the azirine–$Fe_2(CO)_9$ reactions (Table I), subject to the substitution pattern in the hetercycle. Azirines having one or two alkyl groups at the 3 position [**4d**–**g**] gave substantial amounts of the urea complex **6** and the ketone **10**, but little, if any, pyrrole (**8**) or complexes **5**, **7**, and **9**. Azirines lacking alkyl groups at the 3 position [**4a**–**c**] gave pyrroles (**8**) and complexes of structural type **5** as the major products, some urea complex **7**, but little, if any, of the urea complex **6** or ketone **10**. These results can be rationalized as follows: electron-donating alkyl groups will promote dimerization of the nitrene complex **14** to **15** [precursor to **6** and **10**]. For **14**, R′ = R″ = H, addition of **14** to **13** will be favored (path b) thus producing the pyrrole (**8**) and complex **5**.

Of course, in the absence of azirine, the nitrene complex **14** should undergo dimerization to **15**, even when R′ = R″ = H. To determine the validity of this hypothesis and to obtain evidence for C–N cleavage of the azirine ring, 1-azidostyrene


$C_6H_5C(N_3)=CH_2$

was reacted with $Fe_2(CO)_9$. The reactions of several aliphatic and aromatic, but not vinyl, azides[14,15] with iron carbonyls have been described, the results being consistent with a nitrene intermediate, either free or complexed to iron (i.e., analogous to **14**).

The major products of the α-styryl azide–$Fe_2(CO)_9$ reaction were **6a** and **10a**, accompanied by a small quantity of **5a**. Neither pyrrole **8a** nor complexes **7a** or **9a** were detected in this reaction. These results confirm path a as the principal pathway for the reaction of **14** in the absence of azirine or for azirines having alkyl groups at the 3 position. Furthermore, the isolation of several of the same products using α-styryl azide or azirines as reactants supports the proposed C–N bond cleavage of the azirine ring.

In conclusion, this research has resulted in a novel synthesis of pyrroles and of some interesting organometallic complexes, albeit in low yield. The nature of the azirine has an important influence on the product distribution for the $Fe_2(CO)_9$ reaction. The nature of the metal carbonyl used in reactions with azirines has a very significant effect on the reaction course [$M(CO)_6$ gives **1**–**3**; $Fe_2(CO)_9$ affords **5**–**10**]. Carbon–nitrogen bond cleavage of the heterocycle occurs in the $Fe_2(CO)_9$ reactions. The very different results of the azirine–$M(CO)_6$ [M = Cr, Mo, W] reactions may be a consequence of C–C bond cleavage of **4**. A mechanistic investigation of the latter reaction is currently in progress.

Experimental Section

General Data. Melting points were determined using a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectral determinations were made using a Beckman IR-20A spectrometer. NMR spectra were recorded on a Varian T-60 or HA-100 spectrometer. Mass spectra were recorded on a Varian MS 902 spectrometer. A Perkin-Elmer 202 spectrometer was used for ultraviolet spectra. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn., Instranal Laboratory, Rensselaer, N.Y., The Butterworth Microanalytical Consultancy Ltd., Teddington, Great Britain, and by Drs. F. Pascher and E. Pascher, Bonn, West Germany.

Solvents were purified and dried by standard methods. All reactions were effected under a dry nitrogen atmosphere.

Azirines (4). The 2-arylazirines [**4a**–**c**] were synthesized from the appropriate styrenes, using the procedure of Hortmann and coworkers.[16] 3-Methyl-2-phenyl-1-azirine (**4d**), 3-ethyl-2-phenyl-1-azirine (**4e**), and 2-methyl-3-isopropyl-1-azirine (**4f**) were prepared according to the iodine–azide technique developed by Hassner and co-workers.[17] Azirines **4e** and **4f** are new: **4e**, bp 95–98 °C (12 mm), NMR ($CDCl_3$) δ 0.90 (t, 3H, CH_3), 1.58 (m 2 H, CH_2), 2.25 (t, 1 H, CH), 7.30–8.00 (m, 5 H, C_6H_5); **4f**, bp 58 °C (45 mm), NMR ($CDCl_3$) δ 0.82 (d, 6 H, CH_3), 1.50–1.87 (m, 2 H, –CHCH–), 2.40 (s, 3 H, CH_3).

3,3-Dimethyl-2-phenyl-1-azirine (**4g**) was prepared according to the procedure of Leonard and Zwanenburg.[18]

Reactions of Azirines with $Fe_2(CO)_9$. (i) 2-Phenylazirine (4a). A mixture of 2-phenylazirine [2.34 g, 20.0 mmol] and $Fe_2(CO)_9$[10.9 g, 30.0 mmol] in freshly distilled benzene (100 ml) was stirred at 50 °C for 4 h. The solution was filtered and the filtrate was flash evaporated. The resulting oil was dissolved in the minimum amount of benzene and chromatographed on neutral alumina [Woelm activity grade I]. Elution with benzene first gave **5a** followed by the urea **6a**. Elution with benzene–ether gave **7a** and then the pyrrole **8a**. Elution with ether–chloroform afforded **9a** followed by acetophenone (**10a**). Further purification of **5a**–**10a** was effected by rechromatography of each of the fractions. Pertinent analytical and physical data are listed in Tables I and II.

(ii) 2-(4′-Methylphenyl)-1-azirine (4b). A mixture of **4b** [1.31 g, 10 mmol] and $Fe_2(CO)_9$ [5.45 g, 15 mmol] in benzene [100 ml] reacted, and the reaction mixture was then worked up using the procedure for **4a**.

(iii) 2-(4′-Bromophenyl)-1-azirine (4c). The azirine [2.54 g, 15 mmol] and $Fe_2(CO)_9$ [8.20 g, 22.5 mmol] were reacted, and the reaction mixture was then worked up, following the procedure described for **4a**.

(iv) 3-Methyl-2-phenyl-1-azirine (4d). A mixture of **4c** [1.31 g, 10.0 mmol] and $Fe_2(CO)_9$ [5.45 g, 15.0 mmol] in benzene [100 ml] was stirred at 50 °C for 4 h. After filtration and subsequent flash evaporation, the resulting oil was chromatographed on Florisil. Elution with benzene gave **6d**. Elution with benzene–ether afforded **8d** and then the ketone **10d** which were further purified by rechromatography on Florisil. Additional propiophenone (**10d**) was obtained by Soxhlet extraction of the benzene insoluble solid with chloroform.

(v) 3-Ethyl-2-phenyl-1-azirine (4e). The azirine **4e** [1.45 g, 10 mmol] and $Fe_2(CO)_9$ [5.45 g, 15 mmol] in benzene [100 ml] were reacted, and the reaction mixture was then worked up, analogously to the method for **4d**.

(vi) 2-Methyl-3-isopropyl-1-azirine (4f). A mixture of **4f** [0.80 g, 8.25 mmol] and $Fe_2(CO)_9$[4.48 g, 12.3 mmol] in benzene [100 ml] was reacted, and the reaction mixture was then worked up, as described for **4d**.

(vii) 3,3-Dimethyl-2-phenyl-1-azirine (4g). A mixture of **4g** [2.18 g, 15.0 mmol] and metal carbonyl [8.19 g, 22.5 mmol] in benzene [100 ml] reacted, and the reaction mixture was then worked up, as described for **4d**.

Thermolysis of the Urea Complex, 6g, in Ethanol. A 95% ethanol solution (100 ml) of **6g** [0.750 g, 1.32 mmol] was refluxed for 4 h. The solution was cooled and filtered, and the filtrate was evaporated in vacuo. The resulting oil was crystallized from ether and subsequent recrystallization from ethanol gave 0.350 g [83%] of the divinyl urea **11** as a white solid: mp 156–157 °C; ir (CH_2Cl_2) ν_{CO} 1645 cm^{-1}, ν_{NH} 3450 cm^{-1}; NMR ($CDCl_3$) δ 1.68[s, 6 H, CH_3], 1.73 [s, 6 H, CH_3], 7.23 [s, br; 10 H, aromatic]; mass spectrum m/e 320 [M^+]. Anal. Calcd for $C_{21}H_{24}N_2O$: C, 78.71; H 7.55; N, 8.74. Found: C, 78.44; H, 7.54; N, 9.14.

Reaction of 1-Azidostyrene with $Fe_2(CO)_9$. A mixture of 1-azidostyrene[16] [2.90 g, 20.0 mmol] and $Fe_2(CO)_9$ [10.9 g, 30.0 mmol] in benzene [100 ml] was stirred for 4 h at 50 °C. The solution was cooled and filtered, and the filtrate was flash evaporated. The residue was dissolved in benzene and chromatographed on Florisil. Elution with benzene afforded the urea complex **6a** contaminated with several by-products [fraction A]. Elution with ether gave 95 mg [4.0%] of acetophenone (**10a**). Fraction A was rechromatographed on neutral alumina. Elution with benzene gave 43 mg [0.4%] of $Fe_3(CO)_{12}$, followed by 38 mg [0.7%] of **5a** and 29 mg of an unidentified triiron organometallic complex [mass spectroscopy indicates the presence of an $Fe_3(CO)_9$ group in the complex]. Further elution with benzene or elution with benzene–ether (3:1) gave 0.992 g [18.3%] of the urea complex **6a**.

Acknowledgment. We are grateful to the National Research Council of Canada for support of this research.

Registry No. **4a**, 7654-06-0; **4b**, 32687-33-5; **4c**, 17631-26-4; **4d**, 16205-14-4; **4e**, 51209-52-0; **4f**, 60349-73-7; **4g**, 14491-02-2; **5a**, 60241-42-1; **5b**, 60204-37-7; **5c**, 60204-38-8; **5e**, 60349-65-7; **6a**, 60349-66-8; **6b**, 60349-67-9; **6c**, 60349-68-0; **6d**, 60349-69-1; **6e**, 60349-70-4; **6f**, 60349-71-5; **6g**, 60349-72-6; **7a**, 60204-39-9; **7b**, 60204-40-2; **7c**, 60204-41-3; **8a**, 838-40-4; **8b**, 21399-23-5; **8c**, 55368-36-0; **8d**, 17799-61-0; **9a**, 60204-36-6; **9b**, 60285-58-7; **10a**, 98-86-2; **10c**, 99-90-1; **10d**, 93-55-0; **10e**, 495-40-9; **10f**, 108-10-1; **10g**, 611-70-1; **11**, 60349-74-8; 1-azidostyrene, 16717-64-9; $Fe_2(CO)_9$, 15321-51-4.

References and Notes

(1) (a) A. Hassner, S. S. Burke, and J. Cheng-fan I, *J. Am. Chem. Soc.*, **97**, 4692 (1975); (b) A. Padwa and J. K. Rasmussen, *ibid.*, **97**, 5912 (1975); (c) A. Padwa and N. Kamigata, *J. Chem. Soc., Chem. Commun.*, 789 (1975); (d) N. Gakis, H. Heimgartner, and H. Schmid, *Helv. Chim. Acta*, **58**, 748 (1975); and references cited within these papers.
(2) (a) K. N. Chen, R. M. Moriarty, B. G. De Boer, M. R. Churchill, and H. J. C. Yeh, *J. Am. Chem. Soc.*, **97**, 5602 (1975); (b) S. Sarel, A. Felzenstein, R. Victor, and J. Yovell, *J. Chem. Soc., Chem. Commun.*, 1025 (1974); and references cited within these papers.
(3) H. Alper and S. Wollowitz, *J. Am. Chem. Soc.*, **97**, 3541 (1975).
(4) A preliminary communication has appeared: H. Alper and J. E. Prickett, *J. Chem. Soc. Chem. Commun.*, 191 (1976).
(5) H. Alper, *J. Organomet. Chem.*, **50**, 209 (1973).
(6) D. P. Madden, A. J. Carty, and T. Birchall, *Inorg. Chem.*, **11**, 1453 (1972).
(7) H. Alper, *Inorg. Chem.*, **11**, 976 (1972).
(8) M. Herberhold and K. Leonhard, *J. Organomet. Chem.*, **78**, 253 (1974).
(9) R. L. Jones and C. W. Rees, *J. Chem. Soc. C*, 2249 (1969).
(10) P. S. Braterman, "Metal Carbonyl Spectra", Academic Press, London, 1975.
(11) G. W. Parshall, *Acc. Chem. Res.*, **3**, 139 (1970).
(12) M. M. Bagga, W. T. Flannigan, G. R. Knox, P. L. Pauson, F. J. Preston, and R. I. Reed, *J. Chem. Soc. C*, 36 (1968).
(13) H. Alper and W. G. Root, *J. Am. Chem. Soc.*, **97**, 4251 (1975).
(14) M. Dekker and G. R. Knox, *Chem. Commun.*, 1243 (1967).
(15) C. D. Campbell and C. W. Rees, *Chem. Commun.*, 536 (1969).
(16) A. G. Hortmann, D. A. Robertson, and B. K. Gillard, *J. Org. Chem.*, **37**, 322 (1972).
(17) A. Hassner and F. W. Fowler, *J. Am. Chem. Soc.*, **90**, 2869 (1968); A. Hassner and F. W. Fowler, *J. Org. Chem.*, **33**, 2686 (1968).
(18) N. J. Leonard and B. Zwanenburg, *J. Am. Chem. Soc.*, **89**, 4456 (1967).