(4) Green, M. L. H.; Ishaq, M.; Whiteley, R. N. *J. Chem. Soc. A* **1967,** 1508.
(5) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977,** *99*, 6099.
(6) Davison, A.; Krusell, W.; Michaelson, R. *J. Organomet. Chem.* **1974,** *72*, C7.
(7) Flood, T. C.; DiSanti, F. J.; Miles, D. L. *Inorg. Chem.* **1976,** *15*, 1910.
(8) Riley, P. E.; Capshew, C. E.; Pettit, R.; Davis, R. E. *Inorg. Chem.* **1978,** *17*, 408.
(9) After submission of this manuscript, Gladysz reported the NMR spectral observation of $CpRe(PPh_3)(NO)CH_2^+$: Wong, W.-K.; Tam, W.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979,** *101,* 5441. It is interesting to note that the methylene protons are nonequivalent as they are in **2**; however, even at 10 °C no line broadening is evident and thus the barrier to rotation about the rhenenium–methylene bond must be substantially higher than that observed for **2**.
(10) The ionized ethanol exhibits a broad triplet at δ 1.47 (3 H) and a broad quartet at 4.11 (2 H).
(11) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976,** *20*, 299.
(12) (a) Redhouse, A. D. *J. Organomet. Chem.* **1975,** *99,* C29. (b) Friedrich, P.; Besl, G.; Fischer, E. O. *Ibid.* **1977,** *139*, C68.
(13) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979,** *101,* 585.
(14) For a summary of the slow and fast exchange approximations and the coalescence formula used see Anet, F. A. L.; Bourn, A. J. R. *J. Am. Chem. Soc.* **1967,** *89*, 760.

M. Brookhart,* James R. Tucker
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

Thomas C. Flood,* John Jensen
Department of Chemistry
University of Southern California
Los Angeles, California 90007

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Pressure Effects on the Thermal Cis → Trans Isomerization of 4-Dimethylamino-4′-nitroazobenzene. Evidence for a Change of Mechanism with Solvent

Sir:

The mechanism of the thermal isomerization of *cis*-azobenzenes has attracted considerable interest. The reaction may proceed via rotation about the N=N bond or via inversion of one of the nitrogen atoms. Although a theoretical calculation[1] on unsubstituted azobenzene has supported the inversion mechanism, the experimental results obtained so far have been inconclusive. Thus, the enthalpy of solvent transfer[2] and the activation parameters in cholesteric liquid crystal solvent[3] were taken as evidence for the inversion and the rotation mechanisms, respectively. For push-pull-substituted azobenzenes, large kinetic solvent effects were observed.[4] These results are most likely a reflection of the dipolar rotational transition state expected for these azobenzenes. The two transition states are illustrated in Scheme I for 4-dialkylamino-4′-nitroazobenzene.

Scheme I

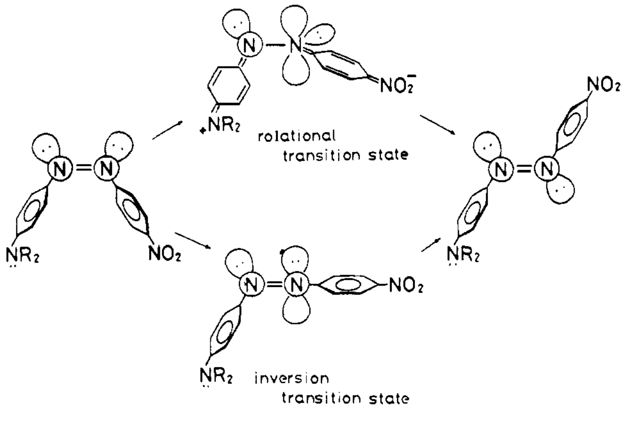

Table I. First-Order Rate Constants for the Thermal Cis → Trans Isomerization of 4-Dimethylamino-4′-nitroazobenzene at Various Pressures

benzene[a] (30 °C)		*n*-hexane[a] (40 °C)	
pressure, bar	10^2k, s^{-1}	pressure, bar	10^2k, s^{-1}
1	1.78	1	1.06
200	2.12	300	1.11
400	2.43	600	1.13
600	2.81	900	1.03
800	3.15	1200	1.06
		1500	1.09
		1800	1.12
		2100	1.19

[a] Solvent.

It is now recognized[5] that the activation volume, obtained from the kinetic effect of pressure according to

$$\Delta V^{\ddagger} = -RT\left(\frac{\partial \ln k}{\partial P}\right)_T \tag{1}$$

is quite sensitive to the polarity change of the reactant(s) during activation. For example, one may expect a fairly strong acceleration by pressure ($\Delta V^{\ddagger} \simeq -10 \sim 20$ cm^3/mol) for the rotational isomerization in the present case. On the other hand, if the inversion mechanism is operative, the pressure increase will cause little change in the rate constant. Accordingly, a high-pressure study has been undertaken for the title compound. The sample solution was contained in an inner glass cell similar to the one described by le Noble and Schlott.[6] The cell was put in a high-pressure vessel with four optical windows set in the cell compartment of a recording spectrophotometer.[7] The solution was irradiated by a filtered light beam from a 150-W tungsten projection lamp after it was brought to a desired temperature and pressure. The thermal decay of the cis isomer was followed after cutting off the irradiation by means of a manually operated shutter.

The results are shown in Table I and Figure 1. The activation volumes at 1 bar are −22.1 cm^3/mol in benzene and −0.7 cm^3/mol in hexane, respectively. The striking difference in pressure effects in the two solvents is totally unexpected. If the reaction proceeds via the rotational transition state, as expected from the solvent effects at 1 bar, the most negative activation volume would be expected for hexane, because the electrostrictive volume contraction is known to increase with decreasing solvent polarity.[8] Therefore, the results presented here suggest quite strongly that the reaction mechanism changes, from inversion in hexane to rotation in benzene. Table II presents the rate constants for unsubstituted azobenzene obtained

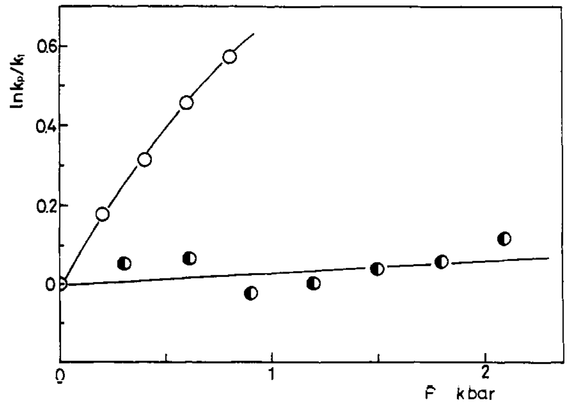

Figure 1. Pressure effects on the first-order rate constant for cis → trans thermal isomerization of 4-dimethylamino-4′-nitroazobenzene: ○, in benzene at 30 °C, ◐, in *n*-hexane at 40 °C.

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Table II. First-Order Rate Constants for the Thermal Cis → Trans Isomerization of Azobenzene at Various Pressures

benzene[a]		*n*-hexane[a]	
pressure, bar	10^4k, s^{-1}	pressure, bar	10^4k, s^{-1}
1	1.00	1	1.23
600	0.99	300	1.28
1200	1.06	600	1.33
1800	1.07	900	1.33
2100	1.10	1200	1.40
		1500	1.43
		1800	1.46
		2100	1.48

[a] Solvent (60 °C).

by a conventional sampling technique. The small pressure effects observed also support the above suggestion since no major polarity change is expected during activation for this compound.

Further experiments with other solvents and with other azobenzenes are in progress.

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References and Notes

(1) S. Ljunggren and G. Wettermark, *Acta Chem. Scand.*, **25**, 1599 (1971).
(2) P. Haberfield, P. M. Block, and M. S. Lux, *J. Am. Chem. Soc.*, **97**, 5804 (1975).
(3) J. M. Nerbonne and R. G. Weiss, *J. Am. Chem. Soc.*, **100**, 5953 (1978).
(4) P. D. Wildes, J. G. Pacifici, G. Irick, and D. G. Whitten, *J. Am. Chem. Soc.*, **93**, 2004 (1971).
(5) T. Asano and W. J. le Noble, *Chem. Rev.*, **78**, 407 (1978).
(6) W. J. le Noble and R. Schlott, *Rev. Sci. Instrum.*, **47**, 770 (1976).
(7) Experimental details will be published in *Rep. Fac. Eng., Oita Univ.*
(8) For example, the activation volume for the [2 + 2] cycloaddition of tetracyanoethylene to butyl vinyl ether becomes more negative with decreasing solvent polarity: F. K. Fleischmann and H. Kelm, *Tetrahedron Lett.*, 3773 (1973).

Tsutomu Asano
Department of Chemistry, Faculty of Engineering
Oita University, 700 Dannoharu, Oita 870-11, Japan

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Carbonyl, Thiocarbonyl, Selenocarbonyl, and Tellurocarbonyl Complexes Derived from a Dichlorocarbene Complex of Osmium

Sir:

The successful coordination of the very reactive molecules carbon monosulfide[1] and carbon monoselenide[2] in transition-metal complexes suggests that it may also be possible to stabilize, through coordination, the unknown molecule carbon monotelluride. Most synthetic routes to carbon monosulfide (or thiocarbonyl) complexes and carbon monoselenide (or selenocarbonyl) complexes involve the use of carbon disulfide (or thiophosgene) and carbon diselenide, respectively. Since the tellurium analogues of these starting materials, i.e., carbon ditelluride and tellurophosgene are also unknown molecules, a new approach was clearly necessary for tellurocarbonyl complexes and this paper describes such an approach which depends upon an unusual dichlorocarbene complex of osmium, $OsCl_2(CCl_2)(CO)(PPh_3)_2$.

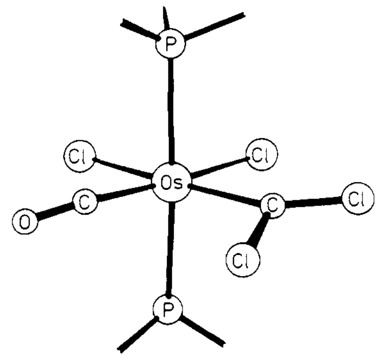


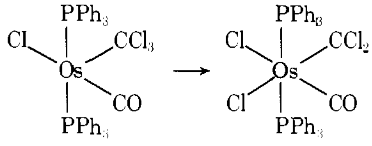
Figure 1. The inner coordination sphere of $OsCl_2(CCl_2)(CO)(PPh_3)_2$.

It is surprising that, although dichlorocarbene was one of the first carbenes to be recognized, no transition-metal complex of this species was reported until 1977.[3] $Fe(TPP)(CCl_2)(H_2O)$ results from the reaction of *meso*-tetraphenylporphyrinatoiron(II) [Fe(TPP)] with carbon tetrachloride in the presence of an excess of reducing agent and the thorough characterization of this molecule includes an X-ray crystal structure determination.[4] This is apparently the only dichlorocarbene complex to have been described, although various monochlorocarbene complexes are known.[5] Our synthesis of an osmium dichlorocarbene complex was a development of earlier work in which we had shown that reaction between $OsHCl(CO)(PPh_3)_3$ and a diorganomercury compound led to a coordinatively unsaturated organo derivative of osmium(II),[6] vis.,

$$OsHCl(CO)(PPh_3)_3 + HgR_2 \rightarrow OsRCl(CO)(PPh_3)_2 + RH + Hg\downarrow + PPh_3$$

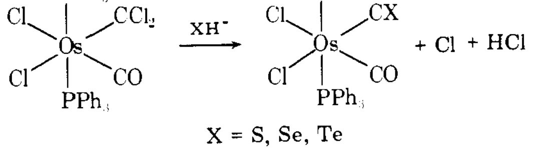
By using this reaction to transfer a trichloromethyl group to osmium, we anticipated that rearrangement of the expected coordinatively unsaturated trichloromethyl intermediate could lead to a dichlorocarbene complex.

In fact, reaction between $OsHCl(CO)(PPh_3)_3$ and $Hg(CCl_3)_2$[7] proceeded to give orange crystals of $OsCl_2(CCl_2)(CO)(PPh_3)_2$ (I) in >80% yield.[8] The dichlorocarbene ligand gives rise to IR bands at 880 (s) and 780 and 770 (m) cm^{-1} which we assign to ν(C–Cl). Fe(TPP)(CCl_2) exhibits ν_{C-Cl} at 872 cm^{-1}.[4] The ^{13}C NMR spectrum ($CDCl_3$, $SiMe_4$) shows, in addition to the signals arising from triphenylphosphine, a peak at 223.2 ppm which is also very close to the signal observed for the carbene carbon in Fe(TPP)(CCl_2).[3] An X-ray structure determination fully confirms the carbene formulation and the structure is shown in Figure 1.[9]



I

I reacts rapidly with primary amines, RNH_2 (R = CH_3, *n*-C_4H_9, *p*-tolyl), to form the isocyanide complexes $OsCl_2(CNR)(CO)(PPh_3)_2$ and slowly with water to form $OsCl_2(CO)_2(PPh_3)_2$.[10] I appears, therefore, to be a perfect precursor of thiocarbonyl, selenocarbonyl, and tellurocarbonyl complexes through reaction with SH$^-$, SeH$^-$,[11] and TeH$^-$,[12] respectively.



X = S, Se, Te

From this reaction thiocarbonyl and selenocarbonyl derivatives resulted in high yield, but the tellurocarbonyl was isolated in only 30% yield after chromatography.[13] This reduced yield is probably associated with the difficulty of preparing

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