[Ir(en)₁]³⁺, the ANU Microanalytical and NMR Services, the Department of Chemistry, the University of Melbourne for use of facilities, and the U.S.-Australia Program for Cooperation in Science for support to carry out the pulse radiolysis studies at Argonne.

Registry No. [Rh(sep)]Cl₃, 86372-67-0; [Rh(diNOsar)]Cl₃, 86372-68-1; [Rh(diAMsarH₂)]Cl₅, 86372-69-2; [Rh(diAMsar)]³⁺, 86372-73-8; $[Ir(sep)]Cl_3, 86372-70-5; [Ir(diNOsar)]Cl_3, 86372-71-6; [Ir(diAM-sarH_2)]Cl_5, 86372-72-7; [Ir(diAMsar)]^{3+}, 86409-32-7; [Ir(en)_3]^{3+},$ 41673-42-1; [Rh(en)₃]³⁺, 16786-61-1; HCHO, 50-00-0; NH₃, 7664-41-7; H₃CNO₂, 75-52-5.

Rates of Chelate Ring Closure in Five-Coordinate Metal Carbonyl Intermediates¹

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Photochemical reactions of (chelate)M(CO)₄ complexes (M = Cr, Mo, W) have been found to proceed via chelate ringopening² or carbonyl loss¹⁻³ depending upon the irradiating wavelength and the identity of the chelating ligand. In several instances, rates of bimolecular reactions of Lewis bases with five-coordinate intermediates formed via carbonyl loss in these and related complexes have been determined.^{1,3} We wish to report studies of $(\eta^2 - NP)M(CO)_4$ (NP = 1-(diphenylphosphino)-2-(diethylamino)ethane; M = Cr, Mo) employing pulsed laser flash photolysis, for which evidence supports chelate ring opening as the predominant photolytic pathway and which provides what are to our knowledge the first rates for unimolecular chelate ring closure in a metal carbonyl intermediate.

The $(\eta^2$ -NP)Mo(CO)₄ substrates, synthesized by means of published methods,⁴ were irradiated at 22 °C by employing a Q-switched Nd:YAG laser (355-nm irradiating frequency, 11-ns FWHI) in Ar-bubbled 1,2-dichloroethane (DCE) or chlorobenzene (CB) containing various concentrations of triisopropyl phosphite (L) as "trapping agent". The decay of the intermediate thus produced was monitored at 475 nm for M = Cr and 420 nm for M = Mo to afford the pseudo-first-order rate constants, k_{obsd} . Figures 1 and 2 exhibit plots of k_{obsd} vs. [L] for both metals and solvents. These data are consistent with the rate law

$$-\mathbf{d}[\operatorname{Int}]/\mathbf{d}t = k_1[\operatorname{Int}] + k_2[\operatorname{Int}][\mathbf{L}]$$
(1)

and with overall mechanism illustrated in the scheme. It is especially significant to note that values of $k_{\rm obsd}$ obtained in the absence of L very closely approximate those obtained through extrapolation of plots of k_{obsd} vs. [L] to [L] = 0, as is expected for a unimolecular ring-closure pathway. Separate studies, involving irradiation of the substrate (M = Mo) at 22 °C employing the 366-nm Hg line (Hanovia 400-W medium-pressure Hg lamp), demonstrated that the Mo-N bond is broken during the ringopening process and that no Mo-CO bond fission takes place. The sole reaction product was found to be $cis(\eta^1-NP)(L)Mo(CO)_4$,



Figure 1. Plots of k_{obsd} vs. [L] for reaction of $[(\eta^1-NP)Cr(CO)_4]$ with triisopropyl phosphite in 1,2-dichloroethane and chlorobenzene at 22 °C.



Figure 2. Plots of k_{obsd} vs. [L] for reaction of $[(\eta^1-NP)Mo(CO)_4]$ with triisopropyl phosphite in 1,2-dichloroethane and chlorobenzene at 22 °C.

Fable I.	Rate Co:	nstants for	Reactions of
(n^1-NP)	M(CO), 1	Intermedia	ates ^a

М	solvent	$10^{-4}k_1$, s ⁻¹	$10^{-4}k_2$, M ⁻¹ s ⁻¹
 Cr	DCE	10.9 (2)	2.7 (3)
Cr	CB	52 (2)	22 (4)
Мо	DCE	4.2 (1)	1.1(2)
Mo	CB	14.6 (1)	7.4 (2)

^a Numbers in parentheses: error limits at the 95% confidence level.

identified through its carbonyl stretching spectrum (ν_{CO} 2017 (m), 1915 (ms), 1895 (s), 1880 (s); DCE solvent).5

Rates of reaction (Table I) differ significantly in DCE and CB, suggesting solvation of the ring-opened intermediate, with subsequent solvent displacement during ring closure or attack at the solvated intermediate by L. The relative rates of both reaction pathways suggest greater solvent-intermediate interaction for the

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⁽⁵⁾ These frequencies compare very favorably to those for closely related cis-L₂Mo(CO)₄ complexes containing two ligands coordinating through P, such as, (diphos)Mo(CO)₄, ν_{CO} (in DCE) 2020 (m), 1919 (s), 1907 (s), 1881 (s), ref 4, but are significantly different from those for the corresponding complexes containing one N and one P donor atom, expected if Mo-P bond fission takes place. Carbonyl stretching frequencies, DCE solvent, for (N-P)Mo(CO)₄ are 2010 (m), 1894 (vs, br), 1844 cm⁻¹.

Scheme I



^a $\hat{NP} = 1$ -(diphenylphosphino)-2-(diethylamino)ethane; M = Cr, Mo.

more polar DCE. Such solvation is consistent with the observed interaction of solvents with such intermediates in low-temperature matrices.6

The relative magnitudes of k_1 and k_2 indicate a preference for unimolecular ring closure to bimolecular attack by L at the solvated intermediate. However, this preference is not as marked as might be expected on the basis of entropy considerations.⁷ Relatively small ratios of k_1/k_2 , determined for reactions in which a bidentate chelating ligand is thermally displaced by various Lewis bases, have been observed in a number of systems,^{8,9} including $(tmen)M(CO)_4$ (tmen = N, N, N', N'-tetramethylethylenediamine; M = Cr, W in their reactions with trialkyl phosphites.¹⁰ Such abnormally small ratios have been attributed to distortions that are induced in the (chelate) $M(CO)_4$ complexes upon ring closure. In several instances the existence of such distortions has been demonstrated through X-ray structural determinations for the complexes.¹¹

Rate constants for both pathways are significantly smaller (1-4 orders of magnitude) than are those that have been reported for bimolecular addition of L to intermediates produced via dissociation of a monodentate ligand from an octahedral complex,^{1,3}

$$(L)_{x}M(CO)_{6-x} \xrightarrow{h_{\nu}} [(L)_{x-1}M(CO)_{6-x}] \xrightarrow{+L'}_{k_{3}} (L)_{x-1}(L')M(CO)_{6-x} (2)$$

This observation further suggests a barrier to ring reclosure and also indicates that there may be significant steric interactions between L and the free end of the bidentate in the path governed by k_2 (Scheme I). These possibilities are under continuing investigation.

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Registry No. I (M = Cr), 18040-40-9; I (M = Mo), 14971-44-9; II (M = Cr), 86273-14-5; II (M = Mo), 86273-15-6; *cis*- $(\eta' - NP)(P(OPr - MO))$ i)₃)Cr(CO)₄, 86273-16-7; cis-(η'-NP)(P(OPr-i)₃)Cr(CO)₄, 86273-17-8.

Synthesis and Structure of a Diarsene: The First Compound with an Unsupported Arsenic-Arsenic **Double Bond**

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The preparation and properties of diphosphenes (RP=PR) are subjects that have attracted the recent attention of several research groups.¹ We now report that by judicious choice of bulky ligands it is possible to isolate compounds featuring double bonds to arsenic.

Our initial approach to diarsene (RAs=AsR) synthesis involving the reductive coupling of $(2,4,6-(t-Bu)_3C_6H_2)AsX_2$ was unsuccessful. The reaction of 2,4,6- $(t-Bu)_3C_6H_2Li$ with 1 equiv of AsCl₃ in THF at -78 °C afforded the heterocycle 1 (mp 146-148 °C)² rather than $(2,4,6-(t-Bu)_3C_6H_2)$ AsCl₂ due to attack



of As on an ortho t-Bu group. Although $(2,4,6-(t-Bu)_3C_6H_2)AsF_2$ (2) (mp 119-121 °C)² can be prepared via the reaction of $2,4,6-(t-Bu)_{3}C_{6}H_{2}Li$ with AsF₃ (THF, -78 °C), 2 fails to yield a diarsene upon treatment with sodium naphthalenide. However, 2 can be reduced to $(2,4,6-(t-Bu)_3C_6H_2)AsH_2$ (3) (mp 146 dec)² by using LiAlH₄ in THF, and treatment of 3 with an equimolar quantity of (Me₃Si)₂CHAsCl₂³ and a 5% excess of DBU (1,5diazabicyclo[5.4.0]undec-5-ene) at 0 °C in THF solution resulted in a white precipitate and an orange-colored supernatant liquid. Filtration followed by chromatographic purification (silica gel/ *n*-hexane) afforded a 72% yield of orange crystalline (2,4,6-(t-1)) $Bu_{3}C_{6}H_{2}As = AsCH(SiMe_{3})_{2}$ (4) (mp 110-113 °C). Preliminary characterization of 4, the first compound with an unsupported arsenic-arsenic double bond,⁴ was accomplished by highresolution mass spectrometry (HRMS) (M⁺ calcd, 554.1726;

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