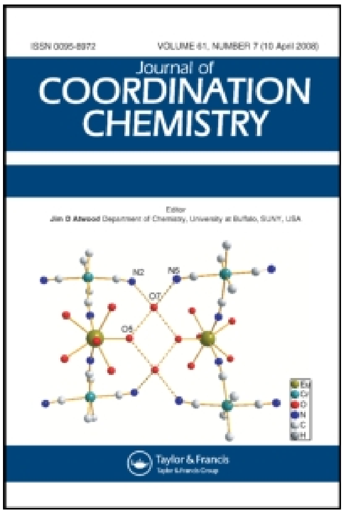

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Octahedral Metal Carbonyls. XXXVI[1] Direct Evidence for the Ring-Opening Mechanism: Substitution Reactions of 2, 2, 8. 8-tetramethyl-3, 7-dithianonanetetracarbonyltungsten (0)

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SHORT COMMUNICATION

Octahedral Metal Carbonyls. XXXVI[1] Direct Evidence for the Ring-Opening Mechanism: Substitution Reactions of 2, 2, 8. 8-tetramethyl-3, 7-dithianonanetetracarbonyltungsten (0)

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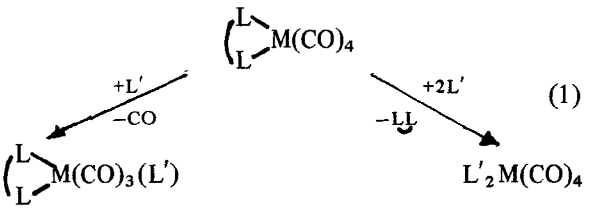
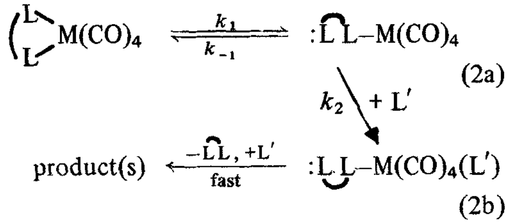
It has been proposed in many instances that substitution reactions of $(L_2)M(CO)_4$ and related complexes (L_2 = chelating bidentate ligand; M = Cr, Mo, W),



(1)

proceed, at least in part, *via* a ring-opening mechanism (2):[1,3–5]



(2a)

(2b)

The rate law (3) is obtained under the assumption of a steady-state concentration of (2-a):

$$\frac{-d[(L_2)M(CO)_4]}{dt} = \frac{k_1 k_2 [(L_2)M(CO)_4][L']}{(k_{-1} + k_2[L'])}. \quad (3)$$

Under reaction conditions usually employed (large excess of L′), the pseudo first-order rate constant, k_{obsd}, is,

$$k_{obsd} = k_1 k_2 [L']/(k_{-1} + k_2[L']), \quad (4)$$

and the "reciprocal relationship",

$$1/k_{obsd} = 1/k_1 + k_{-1}/k_1 k_2 [L'] \quad (5)$$

is applicable. Based on Eq. 4, for $k_{-1} \simeq k_2$, plots of k_{obsd} *vs.* [L′] should exhibit complex behavior, limiting second-order behaviour at low [L′] and limiting first-order behaviour at high [L′]. The reciprocal plot (Eq. 5) is expected to be linear, with intercept $1/k_1$ and slope $k_{-1}/k_1 k_2$. The observation of such rate behaviour has constituted the main line of evidence in support of the ring-opening mechanism,[1,4,5] although activation parameters[3] and the "trapping" of ring-opened species (2a)[6] have also been invoked in its support.

This communication describes the characterization of the first *bona fide* reaction intermediate for a system in which the ring-opening mechanism is to be inferred from kinetic data. The kinetics of the formation and decomposition of this intermediate have also been investigated, and the observations constitute conclusive evidence for the operation of the ring-opening mechanism.

Scans of the high-energy (>2000 cm^{-1}) portion of carbonyl stretching spectra during the course of the reaction of $(DTN)W(CO)_4$ (DTN = 2,2,8,8-tetramethyl-3,7-dithianonane)[5] with $P(OCH_2)_3CCH_3$[7] in xylene (Fig. 1) demonstrate the existence of three carbonyl-containing complexes, the substrate, the reaction product, cis-$[P(OCH_2)_3CCH_3]_2W(CO)_4$[8] and a third species, which was isolated. That species exhibits a carbonyl stretching spectrum characteristic[9] of a *cis*-$L_2M(CO)_4$ complex, (ν(CO):[10] 2031 m, 1921 s, 1905 vs, 1882 ms cm^{-1}; $CHCl_3$ solution). The positions of the absorptions are intermediate to those substrate (ν(CO): 2019 m, 1902 vs, 1883 s, 1848 ms cm^{-1}; $CHCl_3$ solution)[4] and product (ν(CO):

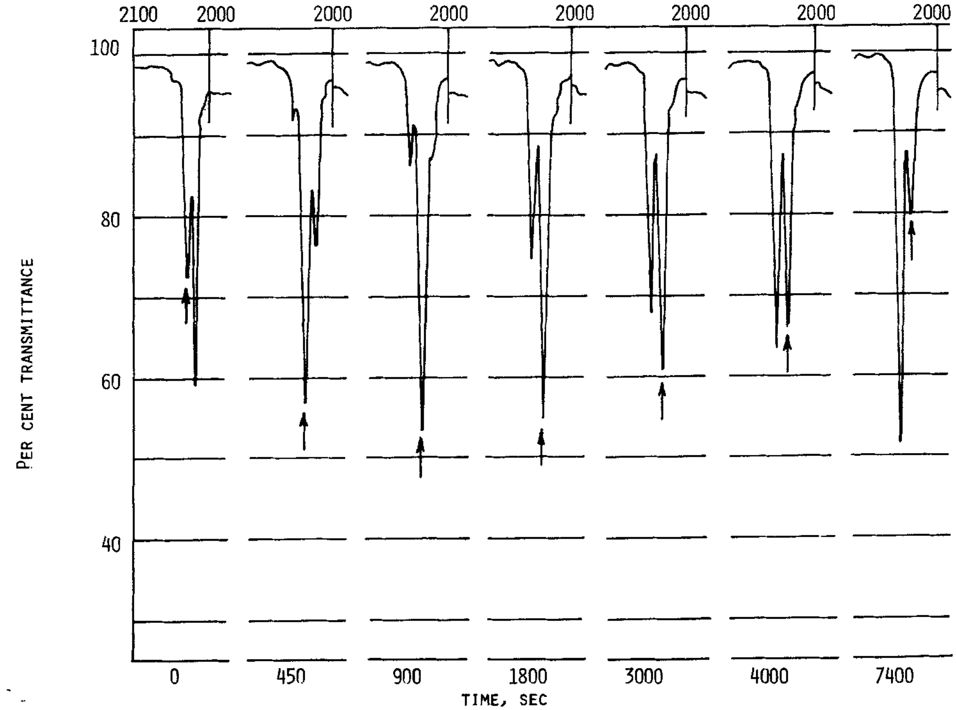


FIGURE 1 Carbonyl stretching spectra (2100–2000 cm^{-1}) for reaction of (DTN)W(CO)$_4$ with P(OCH$_2$)$_3$CCH$_3$ in xylene at 66.5°. Band for the intermediate is indicated by arrow.

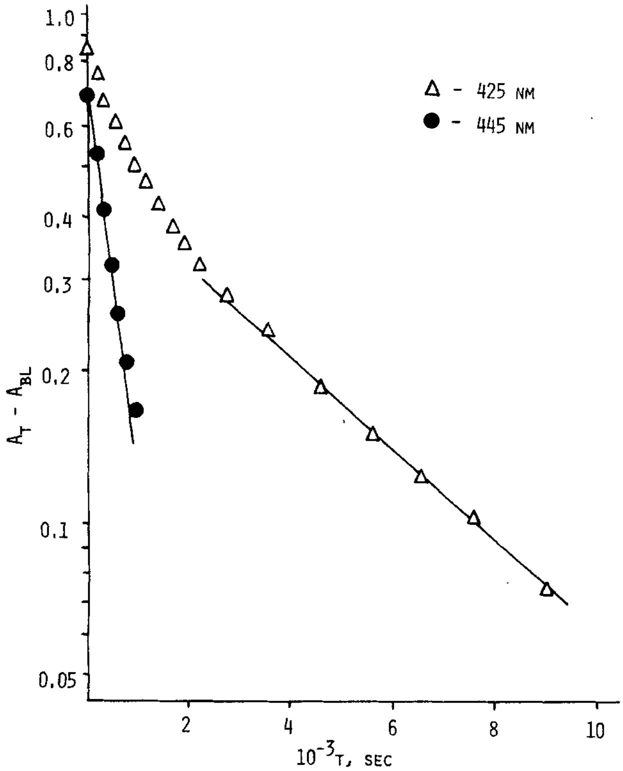


FIGURE 2 Plots of ln(A$_t$ – A$_{bl}$) *vs.* t for reaction of (DTN)W(CO)$_4$ with P(OCH$_2$)$_3$CCH$_3$ in xylene at 66.5° and 425 and 445 nm.

2045 m, 1950 vs, 1924 sh cm^{-1}; CH$_2$Cl$_2$ solution)[8] and indicate it to contain one sulfur and one phosphorous donor atom.[11,12] Its infrared spectrum is very similar to that of (1-diphenyl-phosphino-2-(methylthio)ethane)W(CO)$_4$(ν(CO): 2023 m, 1914 s, 1897 s, 1871 ms cm^{-1}; CHCl$_3$ solution)[12]. Thus it may be concluded on the basis of these data, elemental analysis (±0.3%) and the kinetics results (below) that the species is intermediate (2b), *cis*-(DTN)W(CO)$_4$ [P(OCH$_2$)$_3$CCH$_3$] in which DTN is attached to the metal through a single donor atom.

The visible spectra of substrate, intermediate and product indicate only the substrate and intermediate to absorb at 425 nm, while the substrate is the predominant absorbing species at 445 nm. Typical plots of ln(A$_t$ – A$_{bl}$ *vs.* t (A$_t$ and A$_{bl}$ are absorbances at time t and of a solvent-ligant blank, respectively) for kinetic runs carried out under previously-described conditions[5] for reaction of (DTN)W(CO)$_4$ with P(OCH$_2$)$_3$CCH$_3$ in xylene at 66.5° at the two wavelengths are exhibited in Figure 2. At 445 nm, at which wavelength the substrate is the predominant absorbing species, the plot is linear over about 1.5 half-lives, with the linear portion representing the disappearance of the substrate. At 425 nm, at which wavelength the substrate and intermediate absorb appreciably; the plot exhibits initial curvature and subsequent linearity. The linear portion represents decomposition of the

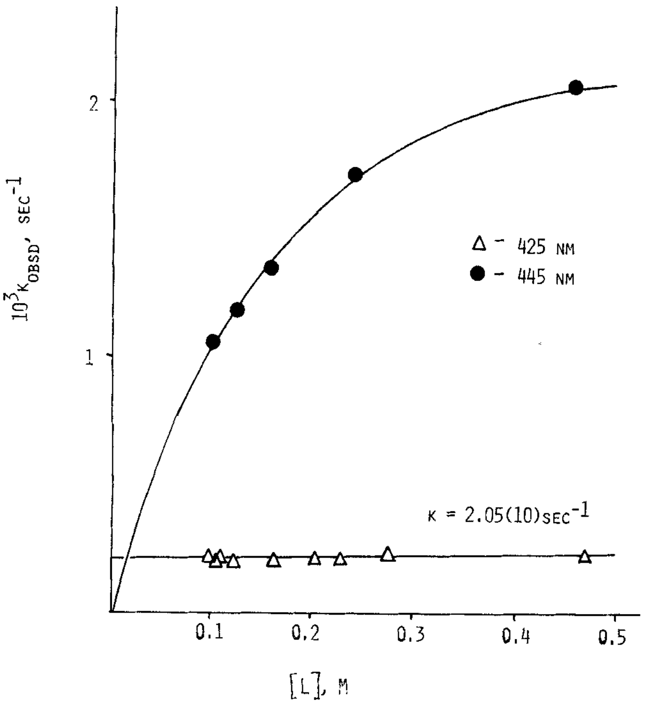


FIGURE 3 Plots of k_{obsd} *vs.* [L] for reaction of (DTN)W(CO)$_4$ with P(OCH$_2$)$_3$CCH$_3$ in xylene at 66.5° and 425 and 445 nm.

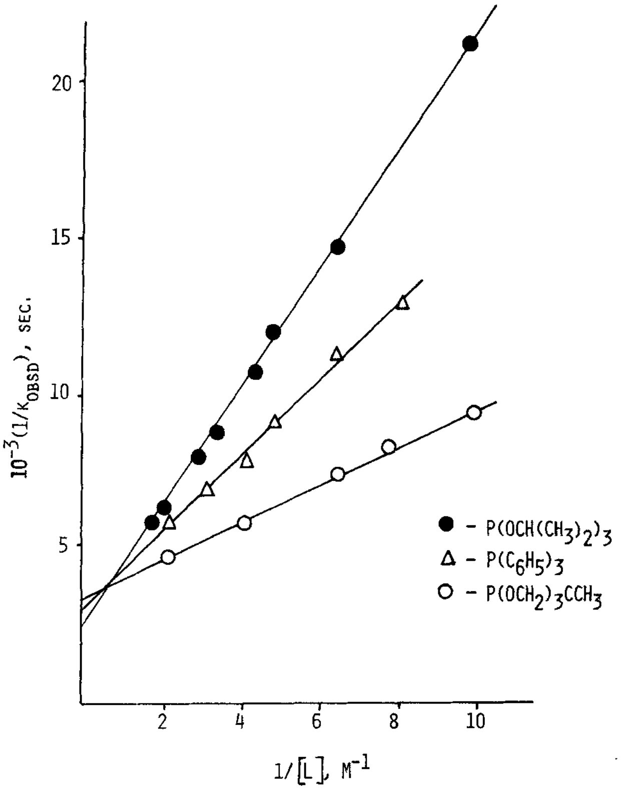


FIGURE 4 Plots of $1/k_{obsd}$ *vs.* 1/[L] for reaction of (DTN)W(CO)$_4$ with various nucleophiles in xylene at 66.5°.

intermediate after disappearance of the substrate. From data at several concentrations of P(OCH$_2$)$_3$CCH$_3$ (in large excess) were obtained plots of k_{obsd} *vs.* [L′] for formation of the intermediate and for its decomposition. The plot of data at 445 nm, illustrated in Figure 3, suggests formation of the intermediate to proceed *via* rate law (3). A linear reciprocal plot ($1/k_{obsd}$ *vs.* 1/[L′], Eq. 5) of these data is also observed (Figure 4). The coincidence of the intercept of this plot with those of data for the reaction of (DTN)W(CO)$_4$ with P(C$_6$H$_5$)$_3$ and P(OCH(CH$_3$)$_2$)$_3$, obtained under identical conditions and for which no intermediate was observed, demonstrates the ring-opening to be a unimolecular process. Decomposition of the intermediate also proceeds *via* a unimolecular process, as is illustrated by the plot of k_{obsd} *vs.* [L′] from data taken at 425 nm (Figure 3).

The data confirm mechanism (2) in every respect. Ring-opening in the substrate is unimolecular. Formation of intermediate (2a) proceeds *via* rate-law (3). The intermediate then undergoes unimolecular decomposition, undoubtedly through rate-determining loss of (S$_2$), to afford, ultimately, the observed *cis*-L′$_2$WCO)$_4$ product.

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