(10) P. E. Eaton, G. R. Carlson, and J. T. Lee, *J. Org. Chem.*, **38**, 4071 (1973).
(11) A. Wolf, German Patent 876237 (May 11, 1953); *Chem. Abstr.*, **52**, 9227*b* (1953).
(12) D. Seebach, *Chem. Ber.*, **96**, 2712 (1963).
(13) A. Schoenberg, J. Bartoletti, and R. F. Heck, *J. Org. Chem.*, **39**, 3318 (1974).
(14) J. E. Bercaw, Private communication.
(15) J. Munch-Petersen, *J. Org. Chem.*, **22**, 170 (1957).
(16) E. B. Womack and J. McWhirter, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., p 714.
(17) Yields and purities are highly susceptible to variations in temperature and stirring efficiency. The reaction is exothermic above 80°, and inefficient stirring in large-scale preparations can lead to very high internal temperatures with reduction in yield and concomitant loss of purity.
(18) A few drops of 6 *N* HCl will also suffice and may result in a cleaner product.[14]
(19) The material is obtained as a mixture of isomers, and extensive purification does not simplify the spectrum. Prominant NMR resonances ($CDCl_3$) are observed at δ 2.45 (q, 2, *J* = 7 Hz), 1.80 (s, 12, broad), 0.98 (t, 3, *J* = 7 Hz).

Contribution from the Department of Chemistry,
Saint Mary's University, Halifax, Nova Scotia, Canada

Kinetics of Isomerization of *trans*-Dicarbonyl Phosphine Complexes of Molybdenum(0) and Tungsten(0)

Clive M. Elson

Received June 11, 1975 AIC50410Q

Recently, electrochemical and x-ray photoelectron spectroscopic studies have been performed to determine the electron distribution within dinitrogen complexes of rhenium,[1,2] molybdenum, and tungsten[3] and their analogues. During the work, preparations of both the cis and trans isomers of dicarbonylbis(1,2-diphenylphosphinoethane)molybdenum(0 and I) and -tungsten(0 and I) were attempted. It was found, however, that only one isomer was stable in a given metal oxidation state, as previously reported.[4-8] The isomerization of *trans*-$[M(CO)_2dpe_2]$ (M = Mo and W, dpe = $Ph_2PCH_2CH_2PPh_2$) has now been monitored electrochemically and the kinetics of the reaction are described here.

The starting materials, *cis*-$[M(CO)_2dpe_2]$ (M = Mo and W), were prepared by published procedures. The dicarbonyl complexes displayed one-electron irreversible oxidation waves (E_{pa} = +0.035 and +0.067 V for M = Mo and W, respectively, vs SCE) when examined by cyclic voltammetry at a vitreous carbon electrode in a CH_2Cl_2–MeOH (10:1 v/v)–0.1 *N* Et_4NBF_4 electrolyte. The irreversibility of the oxidation process is due to the very rapid conversion of *cis*-$[M(CO)_2dpe_2]^+$ (M = Mo and W) to the trans form.[8] Bulk-scale controlled potential oxidations of the cis metal(0) dicarbonyls at +0.2 V on a platinum electrode produced *trans*-$[M(CO)_2dpe_2]BF_4$. The metal(I) salts were characterized by elemental analysis (e.g., calcd for $[W(CO)_2dpe_2]BF_4$: C, 57.2; H, 4.99. Found: C, 57.7, H, 4.27), infrared [single CO stretching frequency at 1860 cm^{-1} (Nujol) for M = Mo and at 1850 cm^{-1} (Nujol) for M = W], conductivity (Λ_M = 32.5 ohm^{-1}/cm^2 for *trans*-$[Mo(CO)_2dpe_2]BF_4$ in 1,2-dichloroethane), and molecular weight measurements (e.g., *trans*-$[Mo(CO)_2dpe_2]BF_4$, expected 518 for a 1:1 electrolyte, found 499).

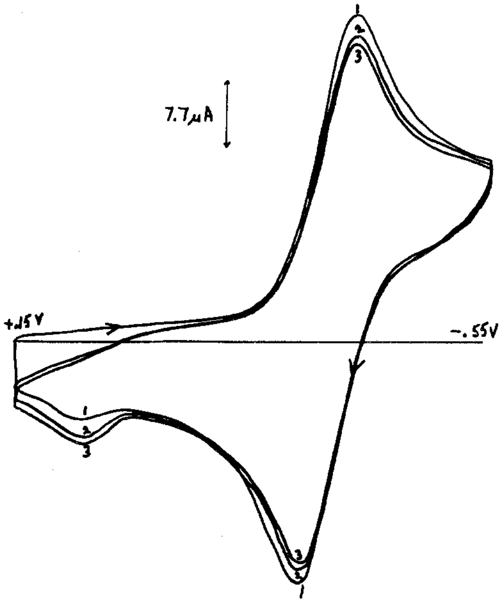

Figure 1. Multicycle voltammogram of *trans*-$[Mo(CO)_2dpe_2]$-BF_4 at a vitreous carbon electrode in CH_2Cl_2–MeOH–0.1 *N* Et_4NBF_4 at $\nu = 0.09 V sec^{-1}$.

Table I. Rate Constants for Isomerization of *trans*-$[M(CO)_2dpe_2]$

trans-[M-$(CO)_2dpe_2$]	Electrolyte	Temp, °C	k, $sec^{-1} \times 10$
M = W	A[a]	20	0.9 ± 0.2
Mo	A	20	0.6 ± 0.1
Mo	A + 5-fold excess dpe	20	0.7 ± 0.2
Mo	A + 15-fold excess dpe	20	0.5 ± 0.1
Mo	Thf-MeOH-LiCl (0.1 *N*)	20	0.3 ± 0.1
Mo	B[b]	11.4	0.36 ± 0.08
Mo	B	11.5	0.34 ± 0.08
Mo	B	11.7	0.42 ± 0.09
Mo	B	19.7	0.70 ± 0.17
Mo	B	28.0	1.4 ± 0.3
Mo	B	27.9	1.3 ± 0.3
Mo	B	38.4	3.2 ± 0.8
Mo	B	38.5	3.1 ± 0.8

[a] A is CH_2Cl_2–MeOH (10:1 v/v)–Et_4NBF_4 (0.1 *N*). [b] B is CH_2Cl–MeOH (10:1 v/v)–Et_4NBr (0.1 *N*).

The metal(I) complexes were reducible at –0.363 and –0.350 V for M = Mo and W, respectively. At high scan rates, the reduction was consistent with a reversible, one-electron, diffusion-controlled, charge transfer.[9,10] However, when the voltage sweep rate was decreased or a multicycle voltammogram was run, a second oxidation wave appeared near 0.0 V (Figure 1). As time elapsed, the height of the second wave increased at the expense of the oxidation wave at –0.28 V. This suggested that the trans metal(0) complexes, generated by reduction, slowly isomerized to the cis configuration. Controlled potential reductions at –0.4 V of *trans*-$[M(CO)_2dpe_2]^+$ (M = Mo and W) produced cis metal (0) dicarbonyls in 100% yields confirming that a geometric rearrangement occurred. An overall reaction scheme can be written:

$$cis\text{-}[M(CO)_2dpe_2] - e \rightarrow trans\text{-}[M(CO)_2dpe_2]^+$$

$$trans\text{-}[M(CO)_2dpe_2]^+ + e \rightleftarrows trans\text{-}[M(CO)_2dpe_2]$$

$$trans\text{-}[M(CO)_2dpe_2] \xrightarrow[slow]{k} cis\text{-}[M(CO)_2dpe_2]$$

where M = Mo and W.

The rate of isomerization (k) was studied by the method of Schwarz and Shain[11] assuming that the reaction was first or pseudo-first order. Double potential step chronoamperograms at –0.15 and –0.5 V were recorded and the ratio of the reduction current of *trans*-$[M(CO)_2dpe_2]^+$ to the oxidation current of *trans*-$[M(CO)_2dpe_2]$ was determined at various times subsequent to the application of the potential. The pulse times varied from 1 to 10 sec and six determinations of k were made from each chronoamperogram and an average was taken.

The isomerization reaction was studied in a variety of electrolytes and at various temperatures (Table I). An Arrhenius plot for the rearrangement of *trans*-$[Mo(CO)_2dpe_2]$ was linear (correlation coefficient = 0.997) and yielded an enthalpy of activation (ΔH^*) of 13.3 ± 0.4 kcal mol^{-1} and a rate constant at 25°C of $1.1 \pm 0.06 \times 10^{-1}$ sec^{-1} by least-squares fitting.[12] The entropy of activation (ΔS^*) was −16 ± 3 cal deg^{-1} mol^{-1} as determined from $k^{25°C}$. The half-lives of the trans molybdenum(0) and tungsten(0) complexes were 10 and 8 sec, respectively, at 20°C.

The similarity of the rate constants and the products of the reaction suggested that both the tungsten and molybdenum complexes reacted by a similar mechanism. Of the two most likely pathways, bond rupture and ligand twist, the latter was ruled out since the cis and trans isomers of $[Mo(CO)_2dpe_2]$ are structurally rigid. George and Siebold[7] have reported that the ^{31}P NMR spectrum of a mixture of the molybdenum(0) isomers displayed separate resonances due to the cis and trans forms only and no intermediate or time-averaged signals were observed between 6 and 40°C.

The rate-determining step in the bond-rupture mechanism involves the intramolecular opening of one of the chelate rings. A dissociative process is in accord with the observed first-order kinetics and is supported by the decreased rate of isomerization of *trans*-$[Mo(CO)_2dpe_2]$ in the tetrahydrofuran (THF) medium. Only if an associative mechanism were operative would the rate constant be expected to increase upon replacing CH_2Cl_2 in the electrolyte with THF since THF is a better ligand for early transition metals than CH_2Cl_2. Moreover, a transition state with a greater charge separation than in the reactant is predicted since the reaction rate decreases as the dielectric constant of the solvent decreases ($\epsilon^{20°C}$ = 7.58[13] and 9.08[14] for THF and CH_2Cl_2, respectively).[15] A metal complex with a dangling phosphine ligand is consistent with an activated complex of increased polarity.

The studies of George and Siebold[7] imply that the rate of isomerization is even slower in benzene (conversion of *trans*-$[Mo(CO)_2dpe_2]$ to the cis form requires 2 hr at 40°C) which agrees with the present results since benzene has a dielectric constant of 2.28 at 20°C.[14] Also, since benzene is a poorly coordinating solvent, the observed differences in rate between the various media cannot be attributed to coordination of the solvents.

The observed entropy of activation may appear to be somewhat negative for a dissociative mechanism. However, Dobson[16] reported that ΔS^* values for substitution reactions involving bond rupture mechanisms of complexes of the type $[W(CO)_4(bidentate)]$ were very dependent upon the nature of the chelating group. For example, the reactions of $[W(CO)_4(bidentate)]$, where bidentate = $(CH_3)_2NCH_2CH_2CH_2N(CH_3)_2$ (tmpa) or $(CH_3)_3CSCH_2CH_2SC(CH_3)_3$ (dto), with P $(OC_2H_5)_3$ proceeded via a reversible dissociation of one end of the bidentate ligand followed by nucleophilic attack of the Lewis base. The activation parameters for the dissociation step were ΔH^* = 31.0 and 25.7 kcal mol^{-1} and ΔS^* = +27.0 and +1.6 cal deg^{-1} mol^{-1} for tmpa and dto, respectively. Furthermore, it was observed that as ΔH^* decreased the values of ΔS^* followed. In the present case the enthalpy of activation is only one-half of that reported for the above reactions. When the bidentate ligand was a phosphine as in $[Mo(CO)_4dpe]$ or $[Mo(CO)_4(H_2PCH_2CH_2PH_2)]$, the substitution reactions with P $(OC_2H_5)_3$ involved dissociation of one of the carbonyl groups (ΔH^* = 38.0 kcal mol^{-1} and ΔS^* = +18.1 cal deg^{-1} mol^{-1})[17] for the former complex while the latter molybdenum complex reacted with rupture of a metal–phosphorus bond (ΔH^* = 32.9 kcal mol^{-1} and ΔS^* = +8.9 cal deg^{-1} mol^{-1}).[18] Although these results provide a good comparison for the present work, nevertheless, a limitation is introduced since the substitution reactions which followed a dissociative mechanism often showed a dependency on the nature of the nucleophile.[16]

A mechanism that involved the total dissociation of a bidentate phosphine ligand from *trans*-$[M(CO)_2dpe_2]$ is unlikely since the reaction rate was unaffected (to within experimental error) by the addition of excess phosphine and since free phosphine ligand was not observed in the NMR spectrum.[7] Also, the dissociation of a carbonyl group seems equally unlikely since the activation parameters are very different from those reported for the loss of CO from other metal carbonyls.[17,19]

If the half-wave potentials of the couples, *cis*-$[M(CO)_2dpe_2]$/*cis*-$[M(CO)_2dpe_2]^+$ and *trans*-$[M(CO)_2dpe_2]$/*trans*-$[M(CO)_2dpe_2]^+$, are estimated from the peak potentials of the cyclic voltammograms ($E_{1/2} = E_p \pm 0.029$ V)[9] and equated to the standard potentials of the couples, then it can be shown that isomerization stabilizes the cis metal(0) complexes with respect to oxidation by approximately 7 kcal mol^{-1}. This stabilization results from the reduced competition for the metal nonbonding electrons by the strongly π-withdrawing carbonyl ligands.

Acknowledgment. The author is indebted to Mr. Peter E. Meadows and Dr. G. J. Leigh for the preparation of the starting materials.

Registry No. *trans*-$[W(CO)_2dpe_2]$, 51202-31-4; *trans*-$[Mo(CO)_2dpe_2]$, 40219-77-0; *trans*-$[W(CO)_2dpe_2]BF_4$, 57049-44-2; *trans*-$[Mo(CO)_2dpe_2]BF_4$, 57049-45-3.

References and Notes

(1) J. Chatt, C. M. Elson, N. E. Hooper, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, in press.
(2) C. M. Elson, *J. Chem. Soc., Dalton Trans.*, in press.
(3) J. Chatt, C. M. Elson, and G. J. Leigh, unpublished results.
(4) J. Lewis and R. Whyman, *J. Chem. Soc.*, 5486 (1965).
(5) P. F. Crossing and M. R. Snow, *J. Chem. Soc.*, 610 (1971).
(6) R. H. Reimann and E. Singleton, *J. Organomet. Chem.*, **32**, C44 (1971).
(7) T. A. George and C. D. Siebold, *Inorg. Chem.*, **12**, 2548 (1973).
(8) F. L. Wimmer, M. R. Snow, and A. M. Bond, *Inorg. Chem.*, **13**, 1617 (1974).
(9) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
(10) P. A. Malachesky, *Anal. Chem.*, **41**, 1493 (1969).
(11) W. M. Schwarz and I. Shain, *J. Phys. Chem.*, **69**, 30 (1965).
(12) Error limits based on standard deviations in least-squares fitting.
(13) F. E. Critchfield, J. A. Gibson, and J. L. Hall, *J. Am. Chem. Soc.*, **75**, 6044 (1953).
(14) "Handbook of Chemistry and Physics", 49th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969, p E59.
(15) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967, p 291.
(16) G. R. Dobson and G. C. Faber, *Inorg. Chim. Acta*, **4**, 87 (1970).
(17) G. C. Faber and G. R. Dobson, *Inorg. Chim. Acta*, **2**, 479 (1968).
(18) G. R. Dobson and A. J. Rettenmaier, *Inorg. Chim. Acta*, **6**, 507 (1972).
(19) G. R. Dobson and E. P. Ross, *Inorg. Chim. Acta*, **5**, 199 (1971).

Contribution from the Chemistry Department,
University of Hawaii, Honolulu, Hawaii 96822

Preparation and Conformation of 1,2-Bis(tetrafluorophosphorano)dimethylhydrazine

Ruth Goodrich-Haines and John W. Gilje*

Received June 13, 1975 AIC50420R

Structures of several compounds which contain P–N–N–P linkages have recently been reported.[1-5] In the P(III) derivatives $P[N(CH_3)N(CH_3)]_3P$ and $F_2PN(CH_3)N(CH_3)PF_2$ x-ray diffraction[1] and NMR evidence,[2] respectively, indicate that the P–N–N–P moieties are planar. This would be consistent with a model in which the two P–N bonds contain considerable pπ–dπ bond character and form a delocalized conjugated π network similar to that found in 1,3-dienes. On the other hand, in the P(V) compounds $OP[N(CH_3)N(C-$