

## The Kinetics and Mechanism of Substitution Reactions of Some Osmium(II)-Dinitrogen Complexes

BY PETER K. MAPLES, FRED BASOLO, AND RALPH G. PEARSON\*

Received August 18, 1970

The rate of molecular nitrogen substitution of  $\text{Os}(\text{N}_2)\text{X}_2\text{L}_3$  ( $\text{L} = \text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ ,  $\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$ ;  $\text{X} = \text{Cl}, \text{Br}$ ) and  $\text{Os}(\text{N}_2)\text{X}_2\text{L}_2\text{L}'$  ( $\text{L} = \text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ ;  $\text{L}' = \text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$ ;  $\text{X} = \text{Cl}, \text{Br}$ ) by phosphorus ligands has been studied in toluene by infrared spectrophotometry. The reactions are first order in complex concentration and independent of ligand concentration. The ranges of the activation parameters for these reactions are  $\Delta H^\ddagger = 27\text{--}34$  kcal/mol and  $\Delta S^\ddagger = 9\text{--}17$  eu. These results are compatible with a dissociative ( $\text{S}_{\text{N}}1$ ) mechanism. Evidence is presented for ligand exchange in the reactions between  $\text{Os}(\text{N}_2)\text{X}_2\text{L}_3$  compounds and certain phosphites. The effect of structural variation on the rate of nitrogen substitution is discussed and a comparison between the dinitrogen compounds studied and their carbon monoxide analogs is made.

### Introduction

Although extensive work has been reported on the kinetics and mechanism of metal carbonyl substitution reactions,<sup>1,2</sup> little quantitative information is available for analogous systems containing coordinated molecular nitrogen.

Numerous molecular nitrogen containing transition metal complexes have been prepared since the initial report of Allen and Senoff.<sup>3</sup> However, in many instances extreme lability of nitrogen, e.g.,  $\text{HCoN}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3$ ,<sup>4</sup> difficulty in purification, e.g.,  $\text{IrX}(\text{N}_2)\text{L}_2$  systems,<sup>5</sup> or inability to vary the appended ligands,  $\text{H}_2\text{RuN}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3$ ,<sup>6</sup> has precluded a simple kinetic study.

Complexes of the type  $\text{Os}(\text{N}_2)\text{X}_2[\text{PR}_2\text{C}_6\text{H}_5]_3$  recently reported by Chatt and his coworkers<sup>7</sup> were chosen for this study, since they represent the only extensive series of characterized isolable compounds in which significant variation of appended ligands has been achieved. Preparation of the carbonyl analogs of the nitrogen compounds has also been reported,<sup>7</sup> although no details were given.

The purpose of this study was to determine the mechanism and to investigate the effect of structural variation on nitrogen substitution reactions. In addition, it was hoped that a quantitative comparison between coordinated nitrogen and the isoelectronic carbon monoxide molecule could be achieved.

### Experimental Section

**Materials.**—Dimethylphenylphosphine, diethylphenylphosphine, tri-*n*-propylphosphine, dimethoxyphenylphosphine, and trimethyl phosphite (Strem Chemicals, Danvers, Mass.) were purified by vacuum distillation. Osmium tetroxide was purchased from D. F. Goldsmith Chemical and Metal Corp., Evanston, Ill., and was used as received. All solvents were re-

fluxed over and distilled from either lithium aluminum hydride or calcium hydride under nitrogen immediately before use.

High-pressure reactions were carried out in a 100-ml Fischer-Porter glass pressure vessel. All other synthetic procedures were carried out under a nitrogen atmosphere employing Schlenk-tube techniques.

$\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3$ ,  $\text{Os}(\text{N}_2)\text{Br}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3$ , and  $\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3$  were prepared by the method of Chatt<sup>7</sup> using initial nitrogen pressures of 80–100 psi.  $\text{OsCl}_3[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$  was prepared according to Douglas and Shaw.<sup>8</sup>

**Preparation of  $\text{OsBr}_3[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$ .**—A mixture of 0.67 g (0.90 mmol) of  $\text{OsCl}_3[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$  and 1.5 g (17.4 mmol) of lithium bromide in 30 ml of ethanol was refluxed for 16 hr. The solution was cooled and the solvent was removed under vacuum. The resulting solid was extracted with dichloromethane and reprecipitated with methanol. Recrystallization of the product from methanol yielded 0.55 g (70%) of purple crystals, mp 168–170°. *Anal.* Calcd for  $\text{C}_{24}\text{H}_{33}\text{O}_2\text{P}_3\text{Br}_3\text{Os}$ : C, 32.89; H, 3.80. Found: C, 33.15; H, 3.92.

**Preparation of  $\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$  (Configuration II).**—A solution of 1.2 g (1.6 mmol) of  $\text{OsCl}_3[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$  in 40 ml of THF was allowed to react with 0.08 g (1.2 g-atoms) of zinc dissolved in 5 ml of mercury under a nitrogen pressure of 85 psi. The initial red color of the solution faded to light yellow with a concurrent drop in nitrogen pressure to a final reading of 73 psi. After 8 hr the reaction vessel was vented, and the solution was filtered and concentrated under vacuum to a 10-ml volume. Addition of 30 ml of methanol caused the precipitation of a white solid. Recrystallization of the crude product from a 1:2 THF–methanol mixture yielded 0.68 g (58%) of white crystals, mp 138–140° dec. *Anal.* Calcd for  $\text{C}_{24}\text{H}_{33}\text{N}_2\text{O}_2\text{P}_3\text{Cl}_2\text{Os}$ : C, 39.19; H, 4.52; N, 3.81; mol wt 735. Found: C, 39.17; H, 4.60; N, 3.75; mol wt 709.

**Preparation of  $\text{Os}(\text{N}_2)\text{Br}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$  (Configuration II).**—A synthetic procedure similar to that given for  $\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$  was used to prepare the bromine-substituted analog. Reaction of 1.6 g (1.8 mmol) of  $\text{OsBr}_3[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$  produced 0.70 g (47%) of white crystals, mp 140–142° dec. *Anal.* Calcd for  $\text{C}_{24}\text{H}_{33}\text{N}_2\text{O}_2\text{P}_3\text{Br}_2\text{Os}$ : C, 34.96; H, 4.04; N, 3.40; mol wt 824. Found: C, 35.38; H, 4.01; N, 3.44; mol wt 816.

**Preparation of  $\text{Os}(\text{CO})\text{Cl}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3$  (Configuration I).**—A solution of 1.3 g (1.8 mmol) of  $\text{OsCl}_3[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3$  in 30 ml of THF, previously saturated with carbon monoxide, was allowed to react with 0.08 g (1.2 g-atoms) of zinc dissolved in 5 ml of mercury. Carbon monoxide was slowly bubbled through the solution for 30 min during which time the color progressively faded from dark red to yellow. The solution was filtered and

(1) R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968), and references cited therein.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 526–625.

(3) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

(4) A. Yamamoto, L. S. Pu, S. Kitazume, and S. Ikeda, *J. Amer. Chem. Soc.*, **89**, 3071 (1967).

(5) J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc. A*, 2841 (1969).

(6) T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **92**, 3011 (1970).

(7) J. Chatt, G. J. Leigh, and R. L. Richards, *Chem. Commun.*, 515 (1969).

(8) P. G. Douglas and B. L. Shaw, *J. Chem. Soc. A*, 334 (1970).

TABLE I  
<sup>1</sup>H NMR DATA FOR OSMIUM(II) COMPOUNDS IN DICHLOROMETHANE<sup>a</sup>

Compound	Confign	P-CH <sub>3</sub> resonance			P-OCH <sub>3</sub> resonance
		τ	Intensity	Multiplicity	
Os(N <sub>2</sub> )Cl <sub>2</sub> [P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ] <sub>3</sub>	II	8.25 (7.8, vct)	8.47 (7.8, vct)	8.77 (9.4, d)	
Os(N <sub>2</sub> )Br <sub>2</sub> [P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ] <sub>3</sub>	II	8.03 (7.9, vct)	8.13 (7.9, vct)	8.60 (9.5, d)	
Os(N <sub>2</sub> )Cl <sub>2</sub> [P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ] <sub>2</sub> P(OCH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	II	8.10 (6.8, vct)	8.13 (8.0, vct)		6.68 (10.5, d)
Os(N <sub>2</sub> )Br <sub>2</sub> [P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ] <sub>2</sub> P(OCH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	II	8.15 <sup>b</sup>			6.71 (10.4, d)
Os(CO)Cl <sub>2</sub> [P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ] <sub>3</sub>	II	8.08 (7.6, vct)	8.23 (7.6, vct)	8.69 (9.1, d)	
Os(CO)Cl <sub>2</sub> [P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ] <sub>2</sub>	I	8.30 (7.3, vct)		8.70 (8.3, d)	
Os(CO)Br <sub>2</sub> [P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ] <sub>3</sub>	II	7.98 (7.8, vct)	8.06 (7.8, vct)	8.59 (9.4, d)	
Os(CO)Br <sub>2</sub> [P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ] <sub>2</sub>	I	8.29 (7.4, vct)		8.52 (7.8, d)	

<sup>a</sup> Chemical shift (*J* in Hz, multiplicity); chemical shift in τ units relative to TMS at τ 10. Multiplicity: d, doublet; vct, virtually coupled triplet. <sup>b</sup> Partially resolved quartet.

the solvent was removed under vacuum. The solid remaining was washed with methanol and recrystallized from a THF-*n*-hexane mixture. This procedure yielded 0.80 g (61%) of yellow crystals, mp 169–170°. *Anal.* Calcd for C<sub>25</sub>H<sub>33</sub>OP<sub>3</sub>Cl<sub>2</sub>Os: C, 42.68; H, 4.73. Found: C, 42.39; H, 4.65.

**Preparation of Os(CO)Br<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> (Configuration I).**—A procedure identical with that given for the preparation of Os(CO)Cl<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> (configuration I) was used to prepare the bromo analog. Reaction of 0.84 g (1.0 mmol) of OsBr<sub>3</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> produced 0.62 g (74%) of yellow crystals, mp 179–180.5°. *Anal.* Calcd for C<sub>25</sub>H<sub>33</sub>OP<sub>3</sub>Br<sub>2</sub>Os: C, 37.89; H, 4.20. Found: C, 37.65; H, 4.18.

**Preparation of Os(CO)Cl<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> (Configuration II).**—The yellow isomer of Os(CO)Cl<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub>, configuration I, 1.4 g (2.0 mmol), was heated to its melting point under nitrogen. After cooling the light yellow solid was recrystallized from a mixture of THF and methanol to give 1.2 g (86%) of white crystals, mp 188–189°. *Anal.* Calcd for C<sub>25</sub>H<sub>33</sub>OP<sub>3</sub>Cl<sub>2</sub>Os: C, 42.68; H, 4.73. Found: C, 42.54; H, 4.62.

**Preparation of Os(CO)Br<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> (Configuration II).**—A synthetic procedure identical with that given for Os(CO)Cl<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> (configuration II) was used to prepare the bromo analog. Isomerization of 0.84 g (1.0 mmol) of Os(CO)Br<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> (configuration I) yielded 0.76 g (90%) of colorless prisms, mp 204–205°. *Anal.* Calcd for C<sub>25</sub>H<sub>33</sub>OP<sub>3</sub>Br<sub>2</sub>Os: C, 37.89; H, 4.20. Found: C, 37.71; H, 4.19.

**Preparation of OsCl<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>2</sub>[P(OCH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]**.—A mixture of 0.20 g (0.28 mmol) of Os(N<sub>2</sub>)Cl<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> and 0.12 g (0.97 mmol) of P(OCH<sub>3</sub>)<sub>3</sub> in 15 ml of benzene was refluxed under nitrogen for 16 hr. The yellow solution was filtered and concentrated to a volume of 5 ml. A solid was obtained by adding *n*-hexane. Recrystallization from benzene-*n*-hexane yielded 0.15 g (68%) of yellow crystals, mp 157–160° dec. *Anal.* Calcd for C<sub>24</sub>H<sub>40</sub>O<sub>6</sub>P<sub>4</sub>Cl<sub>2</sub>Os: C, 33.64; H, 5.13. Found: C, 34.09; H, 5.10.

**Kinetic Measurements.**—Reactions were carried out under nitrogen in a thermostated cell. At timed intervals samples were withdrawn through a side arm equipped with a rubber septum and transferred to a 1-mm NaCl cell. Infrared spectra were recorded with a Perkin-Elmer 337 spectrophotometer coupled to an external recorder. The spectrum of the sample was recorded in the N≡N stretching region (2000–2150 cm<sup>-1</sup>).

Reaction rates were determined under pseudo-first-order conditions by following the disappearance of the coordinated nitrogen stretching vibration. Measurements were performed over a minimum of 2 reaction half-lives. Plots of log (*A* - *A*<sub>∞</sub>) vs. time were linear over the reaction times monitored. The rate constants are considered accurate within the limits ±5%.

Activation parameters were calculated using simple least-squares techniques on the Northwestern University CDC 6400 computer.

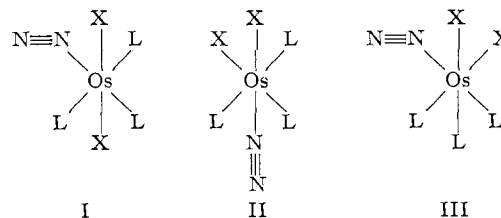
**<sup>1</sup>H Nmr.**—Nmr spectra were obtained with a Varian Associates A-60 spectrometer. Solutions used to monitor the course of a reaction with time were prepared directly in the nmr tube under a nitrogen atmosphere. Peak positions are relative to internal TMS at τ 10. Chemical shift values and coupling constants are considered accurate to ±0.05 τ unit and ±0.05 Hz, respectively.

**Molecular Weights.**—Measurements were performed by Miss H. E. Beck on chloroform solutions at 37° with a Mechrolab Model 302 osmometer.

**Analyses.**—Carbon, hydrogen, and nitrogen determinations were performed in these laboratories by Miss H. E. Beck on an F & M carbon-hydrogen-nitrogen analyzer, Model 185.

## Results

**Structural Assignments.**—Os(N<sub>2</sub>)X<sub>2</sub>[PR<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> and Os(CO)X<sub>2</sub>[PR<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> Complexes.—The stereochemistry of both dinitrogen and carbonyl complexes containing P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> were determined by an analysis of the ligand methyl <sup>1</sup>H nmr resonance patterns (Table I). Similar stereochemistry was assumed for compounds containing P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, since an analysis of their complex resonance patterns was not attempted. The three possible geometric isomers for the nitrogen compounds are given below, where L = P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> or P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> and X = Cl or Br.



Os(N<sub>2</sub>)X<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> complexes in dichloromethane exhibited two methyl resonance patterns consisting of a 1:1 doublet and a multiplet composed of two clearly resolved triplets. Such patterns are commonly encountered in systems containing one unique P(CH<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>5</sub> ligand and two "virtually coupled" *trans*-P(CH<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>5</sub> ligands possessing environmentally nonequivalent methyl groups.<sup>9</sup> The only structure compatible with these data is II which contains no plane of symmetry through the P-Os-P bonds. A similar assignment of structure was reported, but no details were given.<sup>7</sup>

All Os(N<sub>2</sub>)X<sub>2</sub>[PR<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> compounds studied exhibited a single ir-active ν(N≡N) stretching mode in solution (Table II). However, in the solid state a second band appearing as a lower frequency shoulder was recorded.<sup>7</sup>

The methyl nmr patterns of the Os(CO)X<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> compounds prepared at room temperature showed a 1:1 doublet and a single 1:2:1 triplet of relative intensity 1:2. These data indicate configuration I containing a unique P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> ligand and two

(9) W. E. Stancliff and D. G. Hendricker, *Inorg. Chem.*, **7**, 1242 (1968), and references cited therein.

TABLE II  
 INFRARED DATA FOR OSMIUM(II) COMPOUNDS

Compound	Confign	$\nu(\text{C}=\text{O})$ or $\nu(\text{N}=\text{N})$ , $\text{cm}^{-1}$	
		Toluene	Nujol
$\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3$	II	2064 s	2060 s, 2072 sh
$\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3$	II	2080 s	2080 s, 2062 sh
$\text{Os}(\text{N}_2)\text{Br}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3$	II	2091 s	2097 s, 2073 sh
$\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{-P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	II	2122 s, 2117 sh	2099 s, 2076 w
$\text{Os}(\text{N}_2)\text{Br}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{-P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	II	2126 s, 2118 sh	2098 s, 2070 w
$\text{Os}(\text{CO})\text{Cl}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3$	II	1920 s	1912 s
$\text{Os}(\text{CO})\text{Cl}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2$	I	1945 s	1950 s
$\text{Os}(\text{CO})\text{Br}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3$	II	1926 s	1914 s
$\text{Os}(\text{CO})\text{Br}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2$	I	1942 s	1951 s

"virtually coupled"  $\text{trans-P}(\text{CH}_3)_2\text{C}_6\text{H}_5$  groups with a plane of symmetry passing through the P-Os-P bonds.<sup>10</sup>

Thermal isomerization of these species resulted in  $\text{Os}(\text{CO})\text{X}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3$  complexes with  $^1\text{H}$  nmr spectra virtually identical with those of the analogous dinitrogen compounds of configuration II. Similar thermal isomerization has been reported by Shaw, *et al.*,<sup>11</sup> for  $\text{Ru}(\text{CO})\text{X}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3$  compounds. Both carbonyl isomers exhibited a single, broad  $\nu(\text{C}=\text{O})$  band in solution and in the solid state.

#### $\text{Os}(\text{N}_2)\text{X}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$ Complexes.

—The methyl and methoxy resonances of  $\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$  consisted of a clearly resolved set of triplets and a sharp low-field doublet, respectively. These data are only consistent with configuration II where the phosphite ligand is *trans* to chlorine. The spectrum of the bromo analog was similar but the signal due to the "virtually coupled"  $\text{trans-P}(\text{CH}_3)_2\text{C}_6\text{H}_5$  groups was not clearly resolved and appeared as an unsymmetrical quartet.

Splitting of the  $\nu(\text{N}=\text{N})$  band in both solution and the solid state was observed for the phosphite-substituted compounds. A clearly resolved low-intensity band recorded in the solid state appeared as a shoulder in toluene. The presence of what appeared to be two  $\nu(\text{N}=\text{N})$  bands could arise from two terminal dinitrogen moieties present in the same molecule, *e.g.*, a halogen bridged dimer. However, this appears very unlikely on the basis of molecular weight measurements, elemental analysis, and  $^1\text{H}$  nmr data. The second band may be due to a combination band involving the Os-N $\equiv$ N grouping in Fermi resonance with the  $\nu(\text{N}=\text{N})$  fundamental. Similar observations attributable to Fermi resonance have been made in the  $\nu(\text{C}=\text{N})$  region of  $\text{CH}_3\text{C}=\text{N}$  and  $\text{CH}_3\text{C}=\text{N BF}_3$  adducts.<sup>12</sup>

**Kinetic Results.**  $\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3$ .—The rate of displacement of nitrogen from  $\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3$  was measured in toluene by following the decay of the  $\nu(\text{N}=\text{N})$  band at  $2064\text{ cm}^{-1}$ . The rate of reaction was first order in complex concentration and independent of the initial concentration of added ligand. Rate constants were calculated from the slopes of the linear plots of  $\log(A - A_\infty)$  vs. time. Data are collected in Table III.

(10) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).

(11) J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *ibid.*, A, 1787 (1966).

(12) B. Swanson and D. F. Shriver, *Inorg. Chem.*, **9**, 1408 (1970), and references cited therein.

TABLE III

RATES OF REACTION OF  $\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3$  WITH CERTAIN PHOSPHINES AND PHOSPHITES IN TOLUENE

Reagent, L	[L], M	Temp, °C	$10^4k$ , $\text{sec}^{-1}$
$\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$	0.0521	84.0	9.95
$\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$	0.1031	84.0	9.90
$\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$	0.0518	89.0	18.5
$\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$	0.0525	96.0	48.0
$k_{26^\circ} = 6.56 \times 10^{-9}\text{ sec}^{-1}$			
$\Delta H^* = 33.8 \pm 0.6\text{ kcal/mol}$			
$\Delta S^* = 17.3 \pm 1.9\text{ eu}$			
$\text{P}(\text{OCH}_3)_3$	0.0633	65.5	6.98
$\text{P}(\text{OCH}_3)_3$	0.2160	65.5	7.42
$\text{P}(\text{OCH}_3)_3$	0.0630	69.5	13.1
$\text{P}(\text{OCH}_3)_3$	0.0642	74.5	27.2
$\text{P}(\text{OCH}_3)_3$	0.0623	85.0	109
$k_{26^\circ} = 7.60 \times 10^{-8}\text{ sec}^{-1}$			
$\Delta H^* = 33.2 \pm 0.4\text{ kcal/mol}$			
$\Delta S^* = 20.3 \pm 1.2\text{ eu}$			
$\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	0.0510	69.5	14.0
$\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	0.1301	69.5	14.2
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	0.0516	69.5	13.6
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	0.2010	69.5	12.7
$\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$	0.0475	69.5	2.63
$\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$	0.2003	69.5	2.31

The infrared spectrum as a function of time for the reaction of the complex with  $\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$  and  $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$  showed a simple first-order decay of  $\nu(\text{N}=\text{N})$  whereas the reactions with  $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$ ,  $\text{P}(\text{OCH}_3)_3$ , and  $\text{P}(\text{OCH}_2)_3\text{CCH}_3$  produced a second, higher frequency  $\nu(\text{N}=\text{N})$  band which rapidly increased and then slowly decayed (Figure 1). The rate

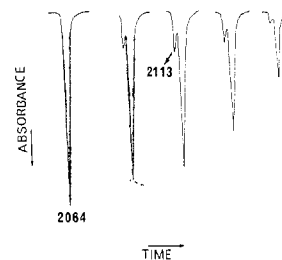


Figure 1.—Infrared spectra of the  $\nu(\text{N}=\text{N})$  region as a function of time for the reaction between  $\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3$  and  $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$  in toluene at  $69.5^\circ$ .

of reaction of the intermediate nitrogen complex was independent of the initial ligand concentration. First-order rate constants for the reaction of the intermediate with additional ligand were calculated by a series of first-order treatments of the experimental data<sup>18</sup> (Table IV).

TABLE IV

RATES OF REACTION OF  $\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3$  AND REACTION INTERMEDIATES WITH VARIOUS PHOSPHITES IN TOLUENE AT  $69.5^\circ$

Reagent, L	[L], M	$10^4k_{\text{complex}}$ , $\text{sec}^{-1}$	$10^4k_{\text{intermed.}}$ , $\text{sec}^{-1}$
$\text{P}(\text{OCH}_3)_3$	0.0631	1.36	9.50
$\text{P}(\text{OCH}_3)_3$	0.1509	1.41	9.21
$\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	0.0520	1.29	9.68
$\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	0.1360	1.32	9.81
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	0.0490	1.40	9.60
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	0.1201	1.39	9.10

(18) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, pp 166-169.

**Os(N<sub>2</sub>)X<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> Complexes.**—The rate of nitrogen displacement from Os(N<sub>2</sub>)Cl<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> and Os(N<sub>2</sub>)Br<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> was measured in toluene by following the decay of the  $\nu(\text{N}\equiv\text{N})$  bands at 2080 and 2091 cm<sup>-1</sup>, respectively. Rate constants calculated from the slopes of the linear plots of log ( $A/A_\infty$ ) vs. time are given in Tables V and VI. The rate

second dinitrogen-containing species during the course of these reactions.

When substitution reactions with P(OCH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> and P(OCH<sub>3</sub>)<sub>3</sub> were monitored by nmr, evidence for the stereospecific replacement of one P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> ligand by a phosphite was obtained. A typical time study of the reaction between Os(N<sub>2</sub>)Br<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> and P(OCH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> is given in Figure 2. Initially the

TABLE V  
RATES OF REACTION OF  
Os(N<sub>2</sub>)Cl<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> WITH VARIOUS PHOSPHINES  
AND PHOSPHITES IN TOLUENE

Reagent, L	[L], M	Temp, °C	10 <sup>3</sup> k, sec <sup>-1</sup>
P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.0480	69.5	7.10
P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.0963	69.5	7.08
P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.0501	74.1	13.2
P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.0498	79.1	25.9
P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.0512	83.0	41.3
$k_{25^\circ} = 6.72 \times 10^{-8} \text{ sec}^{-1}$			
$\Delta H^* = 31.1 \pm 0.3 \text{ kcal/mol}$			
$\Delta S^* = 12.9 \pm 0.8 \text{ eu}$			
P(OCH <sub>3</sub> ) <sub>3</sub>	0.0640	69.5	7.08
P(OCH <sub>3</sub> ) <sub>3</sub>	0.1270	69.5	7.11
P(OCH <sub>3</sub> ) <sub>3</sub>	0.0635	75.0	14.1
P(OCH <sub>3</sub> ) <sub>3</sub>	0.0643	79.2	27.6
P(OCH <sub>3</sub> ) <sub>3</sub>	0.0621	83.0	40.0
$k_{25^\circ} = 7.53 \times 10^{-8} \text{ sec}^{-1}$			
$\Delta H^* = 30.5 \pm 0.3 \text{ kcal/mol}$			
$\Delta S^* = 11.1 \pm 0.9 \text{ eu}$			
P(OCH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.0512	69.5	6.38
P(OCH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.1102	69.5	6.21
P(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.0561	69.5	6.72
P(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.1021	69.5	6.83
P( <i>n</i> -C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub>	0.0622	69.5	6.42
P( <i>n</i> -C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub>	0.1200	69.5	6.58

TABLE VI  
RATES OF REACTION OF Os(N<sub>2</sub>)Br<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> WITH VARIOUS  
PHOSPHINES AND PHOSPHITES IN TOLUENE

Reagent, L	[L], M	Temp, °C	10 <sup>3</sup> k, sec <sup>-1</sup>
P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.0511	69.5	23.4
P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.1010	69.5	22.7
P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.0503	60.2	6.51
P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.0501	65.2	12.7
P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.0521	73.9	40.9
$k_{25^\circ} = 2.57 \times 10^{-7} \text{ sec}^{-1}$			
$\Delta H^* = 30.3 \pm 0.3 \text{ kcal/mol}$			
$\Delta S^* = 13.1 \pm 0.8 \text{ eu}$			
P(OCH <sub>3</sub> ) <sub>3</sub>	0.0632	69.5	23.0
P(OCH <sub>3</sub> ) <sub>3</sub>	0.1890	69.5	23.1
P(OCH <sub>3</sub> ) <sub>3</sub>	0.0612	69.5	23.4
P(OCH <sub>3</sub> ) <sub>3</sub>	0.0620	60.6	7.09
P(OCH <sub>3</sub> ) <sub>3</sub>	0.0618	64.8	12.3
P(OCH <sub>3</sub> ) <sub>3</sub>	0.0641	75.0	49.6
$k_{25^\circ} = 2.54 \times 10^{-7} \text{ sec}^{-1}$			
$\Delta H^* = 30.5 \pm 0.4 \text{ kcal/mol}$			
$\Delta S^* = 13.7 \pm 1.2 \text{ eu}$			
P(OCH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.0540	69.5	22.7
P(OCH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.1300	69.5	22.4
P(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.0531	69.5	22.8
P(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.1008	69.5	22.4
P( <i>n</i> -C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub>	0.0620	69.5	21.7
P( <i>n</i> -C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub>	0.1150	69.5	22.0

of reaction for both complexes was first order in complex and independent of initial ligand concentration. There was no infrared evidence for the presence of a

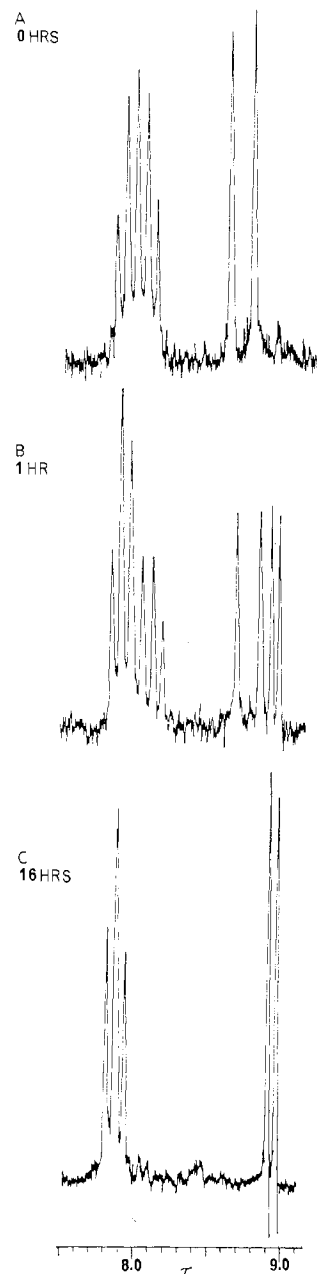


Figure 2.—Selected time-dependent nmr spectra of the reaction between Os(N<sub>2</sub>)Br<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> and excess P(OCH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> in benzene at 69.5°. See text.

spectrum in benzene exhibited the complex resonance at  $\tau$  8.02 of the environmentally nonequivalent trans phosphine methyl group and the doublet at  $\tau$  8.73 of the unique phosphine group trans to bromine. After 1 hr a decrease in the bonded phosphine doublet, the growth of a doublet at  $\tau$  8.92 due to free P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, and an alteration in the trans phosphine resonance pat-

tern was observed. At completion, the reaction solution exhibited a phosphine triplet at  $\tau$  7.85, the free phosphine doublet, and a triplet at  $\tau$  6.40 (not shown) due to the methoxy protons of the bonded phosphite ligands. The three signals were in an area ratio of 2:1:2 indicating a final product of stoichiometry  $\text{OsBr}_2\text{-}[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2[\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5]_2$ . The methyl and methoxy triplets suggest "virtually coupled" trans phosphine and phosphite groups. Additional reaction time, or higher reaction temperatures, resulted in no additional replacement of the two phosphine groups.

No evidence for the liberation of  $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$  was observed by nmr for the reactions with  $\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$  or  $\text{P}(n\text{-C}_3\text{H}_7)_3$ .

**$\text{Os}(\text{N}_2)\text{X}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2[\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5]$  Complexes.**—The rate of nitrogen displacement from  $\text{Os}(\text{N}_2)\text{Cl}_2\text{-}[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2[\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5]$  and  $\text{Os}(\text{N}_2)\text{Br}_2\text{-}[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2[\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5]$  was measured in toluene by following the decay of the  $\nu(\text{N}\equiv\text{N})$  bands at 2122 and 2126  $\text{cm}^{-1}$ , respectively. Rate constants were calculated as described previously and are given in Tables VII and VIII. The rate of reaction for these com-

TABLE VII  
RATES OF REACTION OF  $\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2[\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5]$   
WITH VARIOUS PHOSPHINES AND PHOSPHITES IN TOLUENE

Reagent, L	[L], M	Temp, °C	10 <sup>5</sup> k, sec <sup>-1</sup>
$\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	0.0513	55.3	18.8
$\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	0.1020	55.3	19.0
$\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	0.0513	47.0	5.98
$\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	0.0503	51.0	10.5
$\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	0.0520	58.0	28.5
$\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	0.0532	60.5	37.5

$$k_{25^\circ} = 2.02 \times 10^{-6} \text{ sec}^{-1}$$

$$\Delta H^* = 28.6 \pm 0.4 \text{ kcal/mol}$$

$$\Delta S^* = 11.2 \pm 1.1 \text{ eu}$$

$\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$	0.0485	55.3	19.8
$\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$	0.1020	55.3	19.4
$\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$	0.0520	55.3	19.4
$\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$	0.1200	55.3	19.2
$\text{P}(n\text{-C}_3\text{H}_7)_3$	0.0610	55.3	19.3
$\text{P}(n\text{-C}_3\text{H}_7)_3$	0.1301	55.3	19.0

TABLE VIII  
RATES OF REACTION OF  $\text{Os}(\text{N}_2)\text{Br}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2[\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5]$   
WITH VARIOUS PHOSPHINES AND PHOSPHITES IN TOLUENE

Reagent, L	[L], M	Temp, °C	10 <sup>5</sup> k, sec <sup>-1</sup>
$\text{P}(\text{OCH}_3)_2$	0.0521	40.0	8.40
$\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	0.1120	40.0	8.42
$\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	0.0510	44.9	17.4
$\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	0.0503	50.1	34.9
$\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$	0.0513	54.0	55.9

$$k_{25^\circ} = 9.22 \times 10^{-6} \text{ sec}^{-1}$$

$$\Delta H^* = 26.9 \pm 0.4 \text{ kcal/mol}$$

$$\Delta S^* = 8.7 \pm 1.3 \text{ eu}$$

$\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$	0.5010	40.0	8.39
$\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$	0.1100	40.0	8.41
$\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$	0.0531	40.0	8.46
$\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$	0.1010	40.0	8.43
$\text{P}(n\text{-C}_3\text{H}_7)_3$	0.612	40.0	8.38
$\text{P}(n\text{-C}_3\text{H}_7)_3$	0.1230	40.0	8.41

pounds was first order in complex and independent of initial ligand concentration. A simple first-order decay of the  $\nu(\text{N}\equiv\text{N})$  band was recorded with no evidence for the presence of intermediate dinitrogen complexes.

The nmr spectra of the final reaction products with

$\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$  and  $\text{P}(\text{OCH}_2)_3\text{CCH}_3$  were identical with those of the products from the reactions between the  $\text{Os}(\text{N}_2)\text{X}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3$  compounds and the corresponding phosphite ligands. No evidence for the displacement of either the two  $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$  ligands or the  $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$  ligand was observed in the reactions with  $\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$  and  $\text{P}(n\text{-C}_3\text{H}_7)_3$ .

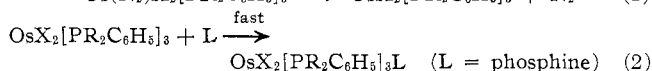
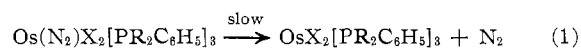
**$\text{Os}(\text{CO})\text{X}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3$  Compounds.**—The displacement of carbon monoxide from the  $\text{Os}(\text{CO})\text{X}_2\text{-}[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3$  (configuration II) compounds was attempted using the phosphine and phosphite ligands employed for the corresponding dinitrogen compounds. The reactions were monitored by observing the intensity of the  $\nu(\text{C}\equiv\text{O})$  band as a function of time. No evidence for carbon monoxide displacement was obtained even under the most stringent reaction conditions. Reaction of the carbonyl compounds with  $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ ,  $\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$ , or  $\text{P}(n\text{-C}_3\text{H}_7)_3$  in decalin at 180° for 16 hr produced no change in the ir spectra of the reaction solution.

Reaction with  $\text{P}(\text{OCH}_3)_3$  or  $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$  at high temperatures, >100°, and long reaction times, >24 hr, resulted in some replacement of the phosphine group trans to the halide, but displacement of the carbonyl group was not observed.

### Discussion

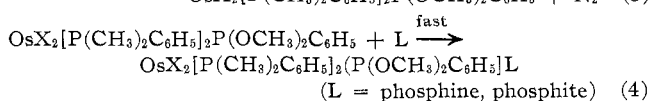
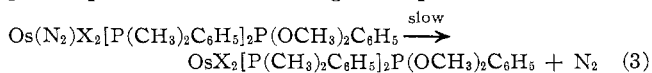
The mechanism(s) of molecular nitrogen displacement from the  $\text{Os}(\text{II})$  compounds studied can best be explained on the basis of an  $\text{S}_{\text{N}}1$  dissociative process with the added complication of phosphine ligand substitution in some systems.

**Systems Involving No Ligand Replacement.**—The reaction of  $\text{Os}(\text{N}_2)\text{X}_2[\text{PR}_2\text{C}_6\text{H}_5]_3$  compounds with the  $\text{PR}_2\text{C}_6\text{H}_5$  ligand coordinated to the starting complex followed a first-order rate law. The most plausible mechanism consists of a rate-determining dissociation of the nitrogen molecule (eq 1) followed by rapid addition of the phosphine ligand (eq 2). Both the enthalpy of ac-



tivation values and the positive entropies of activation are consistent with a dissociative activation step. The enthalpy of activation (28 kcal/mol) reported<sup>14</sup> for the dissociation of nitrogen from the  $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$  ion is very close to that found for the  $\text{Os}(\text{II})$  compounds studied here.

A similar first-order rate law was followed for the displacement of nitrogen from  $\text{Os}(\text{N}_2)\text{X}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{-}[\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5]$  complexes indicating an  $\text{S}_{\text{N}}1$  mechanism (eq 3 and 4). Reaction with either phosphines or phosphites proceeded without ligand replacement as far as



could be determined from product analysis and ir and nmr spectral techniques.

Activation parameters and rate constants for the above processes are collected for comparative purposes in Table IX. It is evident from these data that the ef-

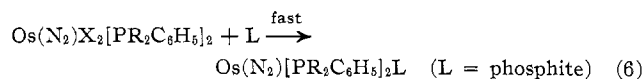
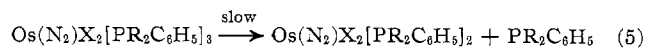
TABLE IX  
KINETIC DATA FOR THE REPLACEMENT  
OF N<sub>2</sub> IN Os(N<sub>2</sub>)X<sub>2</sub>L<sub>2</sub>L' IN TOLUENE

X	L	L'	10 <sup>3</sup> k <sub>25</sub> <sup>o</sup> , sec <sup>-1</sup>	ΔH*, kcal/mol	ΔS*, eu
Cl	P(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	P(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.65	33.8	17.3
Cl	P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	6.72	31.1	12.9
Br	P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	25.7	30.3	13.0
Cl	P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	P(OCH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	202	28.6	11.2
Br	P(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	P(OCH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	922	26.9	8.7

fect of variation of the ligand group cis to the nitrogen molecule is significantly greater than variation in the trans halide group. Replacement of a phosphine ligand by P(OCH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> in Os(N<sub>2</sub>)Cl<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> increases the rate of nitrogen displacement 30-fold, whereas substitution of Br for Cl increases the rate by a factor of only 4. Chatt and coworkers<sup>5</sup> recently reported that changes in ν(N≡N) in IrX(N<sub>2</sub>)L<sub>2</sub> compounds are greater for substitution in the cis phosphine than in substitution of the trans anion. These results are in agreement with our kinetic results if one accepts that change in ν(N≡N) reflects change in the bonding between nitrogen and the metal atom.

The ease of nitrogen displacement as a function of the appended phosphorus ligands follows the order P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> < P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> << P(OCH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>. This trend parallels the commonly accepted order of decreasing basicity and increasing back-bonding capability.<sup>15</sup> Thus, as the electron density on the metal atom decreases, a corresponding decrease in the amount of electron back-donation to the N<sub>2</sub> π\*-antibonding orbital and decrease in the nitrogen-metal bond strength are expected. Although ligand steric factors may play a part in influencing the rate of dissociation, a steric acceleration with increasing bulkiness of the phosphine ligand was not observed.

**Systems Involving Ligand Replacement.**—Evidence for phosphine substitution in the reaction between Os(N<sub>2</sub>)X<sub>2</sub>[PR<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> species and certain phosphites was found by both nmr and ir techniques. In the case of Os(N<sub>2</sub>)Cl<sub>2</sub>[P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub>, direct observation of a second ν(N≡N) band indicated the presence of an intermediate nitrogen complex. The first-order rate law for the disappearance of starting complex and the detection of an intermediate suggests a mechanism involving a rate-determining dissociation of a phosphine group (eq 5), then rapid addition of the phosphite ligand (eq 6) with subsequent rapid dissociation of nitrogen from the phosphite-substituted complex (eq 3 and 4).



Direct observation of intermediates in the reactions between Os(N<sub>2</sub>)X<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> and phosphites was not made. However, the detection of free P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> by nmr during the course of reaction provided evidence for ligand exchange. In an effort to support the possible existence of a phosphite-substituted intermediate, phosphite-containing dinitrogen compounds were synthesized. Unfortunately, only P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>-substituted species could be prepared.<sup>8</sup>

As has been mentioned previously, the reaction of Os(N<sub>2</sub>)X<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>2</sub>P(OCH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> with phosphites was 30–40 times faster than the corresponding reaction with the all-P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>-substituted compound. This difference in relative rate can account for the inability to detect a phosphite-substituted intermediate by ir, since the steady-state concentration would be small.

The rate of disappearance of the ν(N≡N) band of Os(N<sub>2</sub>)X<sub>2</sub>[P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> when treated with phosphites was virtually identical with the simple displacement reaction employing P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>. Thus simultaneous nitrogen dissociation and ligand substitution may be occurring in these systems. In contrast, simple nitrogen displacement from Os(N<sub>2</sub>)Cl<sub>2</sub>[P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> proceeded at one-tenth the rate of ligand replacement by phosphite.

Ligand replacement may be occurring when Os(N<sub>2</sub>)Cl<sub>2</sub>[P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> is treated with P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, since the rate of disappearance of the ν(N≡N) band is greater than that for the corresponding reaction with P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>. However the complexity of the nmr spectrum of a reacting system prevented a clear identification of free P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>.

A quantitative comparison between substitution reactions of the dinitrogen compounds studied and their carbonyl analogs was not possible. Attempts to displace carbon monoxide from Os(CO)X<sub>2</sub>[PR<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>3</sub> compounds even under the most extreme conditions were unsuccessful. These results represent convincing evidence that carbon monoxide is bound more strongly to the metal atom than the relatively labile nitrogen. Similar conclusions have been drawn from comparison of the relative thermal stabilities and qualitative labilities for Fe,<sup>16</sup> Ir,<sup>5</sup> and Ru<sup>16</sup> compounds in which both the carbonyl and dinitrogen compounds have been prepared.

**Acknowledgment.**—This work was supported by the U. S. Atomic Energy Commission under Grant At(11-1)-1087. We thank the Mathey-Bishop Co. for a gift of osmium.

(15) W. D. Horrocks and R. C. Taylor, *Inorg. Chem.*, **2**, 723 (1963).

(16) G. M. Bancroft, M. J. Mays, and B. E. Prater, *Chem. Commun.*, 595 (1960).