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STERIC EFFECTS OF PHOSPHORUS LIGANDS: *cis/trans* DISTRIBUTIONS OF $W(CO)_4L_2$ PRODUCTS

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Summary

The *cis/trans* product distribution in the reaction of phosphines with $W(CO)_4(Me_2N(CH_2)_3NMe_2)$ depends on ligand size; the smaller the ligand the greater the *cis/trans* ratio. The ratios range from 2.9 to 0 for PPh_2Me and $P(o\text{-Tol})_3$, respectively.

Introduction

The importance of phosphorus ligand steric effects in transition metal complexes has received considerable attention during recent years [1—6]. In this report, the effect of ligand size on the *cis/trans* product distributions of reaction 1 is unambiguously demonstrated (tmpa = *N,N,N′,N′*-tetramethyl-1,3-propanediamine and L = a phosphorus ligand).

$$W(CO)_4\text{tmpa} + 2\ L \rightarrow cis \text{ and } trans\text{-}W(CO)_4L_2 + \text{tmpa} \qquad (1)$$

To observe steric effects only, it is necessary to choose ligands which have very similar electronic properties since both σ-donating and π-accepting abilities of ligands can affect stereochemistries [7—9]. The ligand series PPh_2Me, PPh_2Et, PPh_2i-Pr and PPh_2t-Bu provides for increasing size (cone angles of 136°, 140°, 150° and 157°, respectively) [1], while maintaining nearly identical electronic properties. Values for the $\nu(CO)$ A^1 mode of $Ni(CO)_3L$ complexes, used by Tolman as the electronic parameter for phosphorus ligands [1], are within experimental error for PPh_2Me (2067.0 cm^{-1}) and PPh_2Et (2066.7 cm^{-1}) [10]. Although corresponding values are not available for PPh_2i-Pr and PPh_2t-Bu, the electronic similarity of these ligands to PPh_2Et can be seen from other data. Grim and coworkers have found $^1J(^{31}P—^{183}W)$ values and $\nu(CO)$ bands in $W(CO)_5L$ complexes to be indicative of electronic properties [11]. Coupling constant values for the latter three ligands are identical at 240 Hz and the $\nu(CO)$ frequencies are extremely consistent [12].

Results and discussion

For the study reported here, a fivefold excess of each of the ligands PPh_2Me, PPh_2Et, PPh_2i-Pr, PPh_2t-Bu, PPh_3, P(*p*-Tol)$_3$ and P(*o*-Tol)$_3$ was allowed to react with W(CO)$_4$tmpa at 40°C. Completion of reaction was determined by the lack of intense ν(CO) bands characteristic of starting material complex. As reported previously [13], no evidence for *cis/trans* interconversion was observed, even after two weeks at 40°C. Since selective loss of one isomer during purification was a concern, ^{31}P NMR spectra were obtained directly from untreated product solutions. No difficulty was encountered in identifying product peaks. In fact, the spectra of PPh_2Me and PPh_2Et displayed no discernable absorptions other than free ligand, *cis* and *trans* complexes and their ^{183}W satellite peaks. The percentage of *cis* and *trans* complexes, determined by integration of the ^{31}P spectra, are listed in Table 1. Also included are results obtained in a similar manner for PPh_3, P(*p*-Tol)$_3$ and P(*o*-Tol)$_3$.

The results for PPh_2Me, PPh_2Et, PPh_2i-Pr, and PPh_2t-Bu unambiguously indicate the general trend of increasing ligand size producing increased amounts of *trans* product. This is the first known report of its kind. The effect of ethyl replacement for methyl is particularly dramatic. The reason for experimentally identical results for PPh_2Et and PPh_2i-Pr is unclear. That apparent enigma is being investigated further.

Results for PPh_3, P(*p*-Tol)$_3$ and P(*o*-Tol)$_3$ provide further verification of steric effects. Although these three ligands are not electronically identical, as reflected in the slightly different *cis/trans* distributions for the sterically similar ligands PPh_3 and P(*p*-Tol)$_3$ (the cone angle for both is 145° [1]), the extremely large P(*o*-Tol)$_3$ ligand (cone angle 194° [1]) precluded any *cis* complex formation.

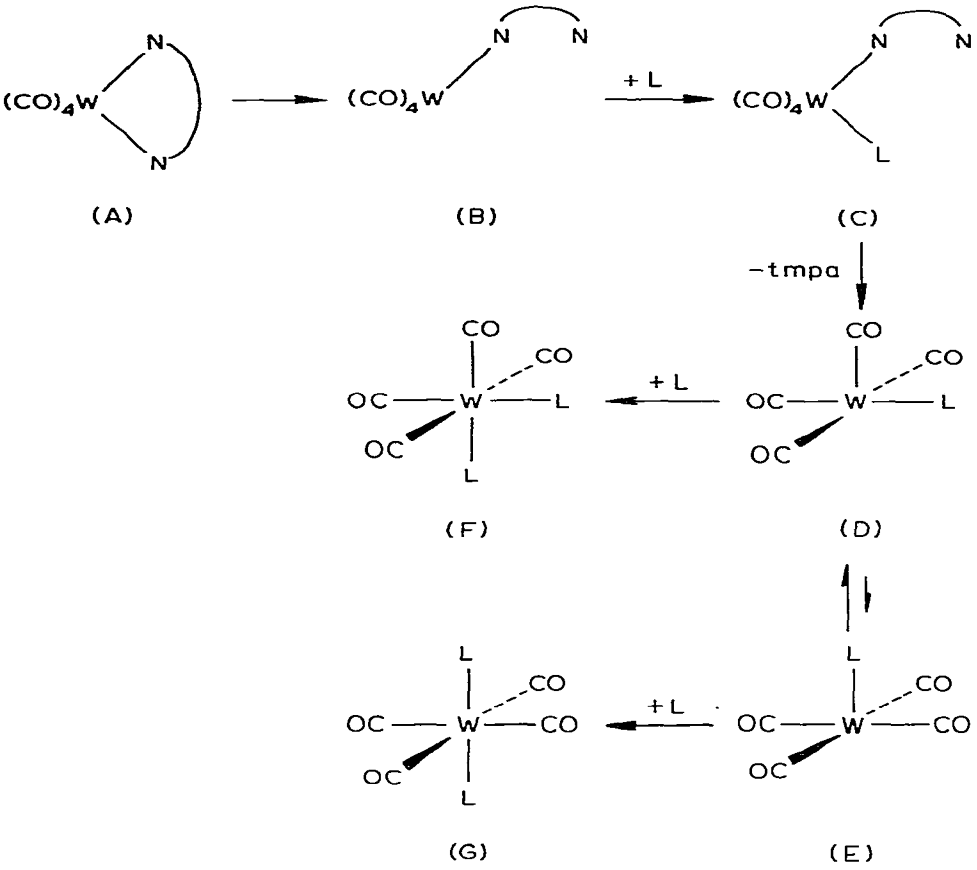
A composite reaction mechanism is depicted below. From observed rate data, the reaction has been shown to proceed through the steps A → B → C → products [13]. Precedence for a square pyramidal intermediate (e.g., D and/or E) comes from matrix isolation studies [14], while Darensbourg et al. [13] have suggested the equilibrium between D and E which produces *cis* (F) and *trans* (G) products, respectively.

TABLE 1

^{31}P CHEMICAL SHIFTS [a] AND *cis/trans* PRODUCT DISTRIBUTION OF W(CO)$_4$L$_2$

Ligand	*cis*		*trans*	
	δ(ppm)	%	δ(ppm)	%
PPh_2Me	−6.44	74	−0.31	16
PPh_2Et	8.93	38	15.41	62
PPh_2i-Pr	22.01	38	29.05	62
PPh_2t-Bu	31.68	21	43.54	79
PPh_3	19.83	23	24.82	77
P(*p*-Tol)$_3$	17.30	21	22.25	79
P(*o*-Tol)$_3$	—	0	32.83	100

[a] Referenced to 85% H_3PO_4; positive values are downfield.



Inclusion of the equilibrium step was based on two studies reported by the latter authors. The reaction of *cis*-$(C_5H_{10}NH)(PPh_3)W(CO)_4$ with ^{13}CO resulted in stereospecific enrichment to yield *cis*-$(^{13}CO)(PPh_3)W(CO)_4$, whereas reaction 1 with L = PPh_3 provided approximately 80% *trans*-$(PPh_3)_2W(CO)_4$ [13]. The results were rationalized in terms of the "site preference" model of Atwood and Brown [7]. Thus, the basal intermediate (D) is believed to be more stable thermodynamically, but steric interactions between the coordinated PPh_3 and a second, incoming PPh_3 ligand result in preferential attack of the apical intermediate (E) [13]. The results reported here are consistent with this hypothesis.

Experimental

General

All reactions, distillations and transfers were carried out in a nitrogen atmosphere. Benzene was stored over 4A molecular sieves and purged with nitrogen prior to use. *N*,*N*,*N′*,*N′*-tetramethyl-1,3-propanediamine (tmpa) was purchased from Aldrich Chemical Co., Inc., and distilled from KOH just prior to use. Tungsten hexacarbonyl, t-butyldiphenylphosphine, tri-*o*-tolylphosphine, tri-*p*-tolylphosphine, and triphenylphosphine were purchased from Strem Chemicals, Inc., and used as received. Methyldiphenylphosphine, ethyldiphenylphosphine, and i-propyldiphenylphosphine were synthesized by literature procedures [15]. $W(CO)_4$tmpa was synthesized using the method reported by Dobson and Faber [16].

IR spectra were recorded using a Beckman 4250 spectrophotometer. The ^{31}P NMR spectra were recorded at 60.8 MHz using an NT-150 instrument operating with a 90° pulse angle and 12 mm probe. Trimethylphosphate was used as an external standard and deuteriobenzene (20% by volume) as the internal lock. NMR spectra were recorded directly on the reaction solutions. Isomer distributions were obtained by integration of the ^{31}P resonances. Chemical shifts, presented in Table 1, are reported relative to 85% H_3PO_4 with downfield shifts assigned positive values. The downfield signals, which also displayed the larger $^1J(WP)$ values, were assigned to the *trans* complexes [17—21]. The IR spectra were also consistent with these assignments.

Reactions

Benzene was used as a solvent for the reactions involving the solid ligands, PPh_3, $P(p\text{-Tol})_3$, and $P(o\text{-Tol})_3$. The liquid alkyldiphenylphosphine ligands were allowed to react with $W(CO)_4$tmpa in the absence of solvent. For the solid ligands, reactions were carried out using ca. 0.045 g and 0.30 g of $W(CO)_4$tmpa and phosphine, respectively, in 20 ml of benzene. All reactions involving the liquid ligands utilized ca. 0.16 g and 0.85 g of $W(CO)_4$tmpa and phosphine, respectively. For example, 0.0467 g (0.110 mmol) of $W(CO)_4$tmpa with 0.3225 g (1.059 mmol) of $P(o\text{-Tol})_3$ and 0.1661 g (0.390 mmol) of $W(CO)_4$tmpa with 0.9036 g (4.218 mmol) of PPh_2Et were reacted. All reactions were carried out at 40°C for 48 h. After the reaction period, the IR spectra showed $\nu(CO)$ bands characteristic of only *trans* and *cis* $W(CO)_4L_2$ products.

Acknowledgments

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