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Preliminary communication

A CALORIMETRIC STUDY OF STERIC EFFECTS IN THE REACTIONS OF PHOSPHORUS LIGANDS WITH $Ni(COD)_2$

C.A. TOLMAN*, D.W. REUTTER and W.C. SEIDEL

*Central Research and Development*** *and Polymer Intermediates Departments, E.I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898 (U.S.A.)*

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Summary

A calorimetric study of the reactions of various phosphorus ligands (and t-BuNC) with di-1,5-cyclooctadienenickel shows that both the extent of reaction and mean Ni—P bond strengths tend to decrease with increasing ligand size. The steric strain energies in various NiL_4 complexes and ΔG for their formation from nickel metal are estimated.

It has become apparent in recent years that steric effects of phosphorus ligands are extremely important, and in many cases dominate the chemistry of transition metal complexes containing them [1]. Here we report a calorimetric study which allows the estimation of steric strain energies in NiL_4 complexes.

Reactions were carried out under N_2 in a Vacuum Atmospheres, Inc. dry box, using a Guild Corp. Model 400 solution calorimeter with a base-line compensator. In a typical run, made in duplicate, six to ten portions of neat ligand were added to 0.4 mmol $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) in 200 ml N_2 purged toluene at about 25°C. In some cases, where the ligand was either very viscous (e.g. $P(OPh)_3$) or a solid (PPh_3), portions of 0.8 *M* L were added from a 5 ml gas tight Hamilton syringe with a water jacket thermostatted at 25.0°C. Typical calorimetric titration curves are shown in Fig. 1.

The enthalpy change (ΔH_1) for the decomposition of $Ni(COD)_2$ by reaction 1 was determined to be -3 ± 1 kcal/mol by adding catalytic amounts of CCl_4 to

$$Ni(COD)_2 + \Delta H_1 \rightarrow Ni(s) + 2\,COD \qquad (1)$$

toluene solutions of $Ni(COD)_2$. Metallic Ni precipitated as a mirror or powder depending on the concentration of added CCl_4***.

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[*] Author to whom correspondence should be addressed.

[**] Contribution No. 2405.

[***] The heat evolved depended somewhat on the amount of CCl_4 used. In decomposing 0.25 mmol $Ni(COD)_2$ with 0.02, 0.10 and 0.31 mmol CCl_4 in separate runs, the measured ΔH's were 2.8, 3.4 and 3.9 kcal/mol respectively. Less CCl_4 gave a slower reaction and better Ni mirror.

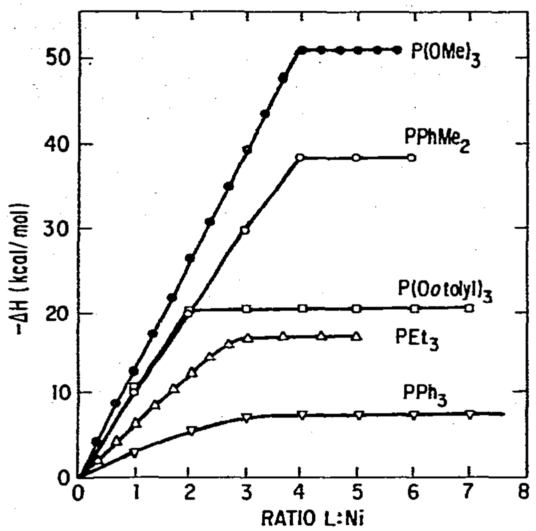

Fig. 1. Calorimetric titrations adding ligands to $Ni(COD)_2$ in toluene at 25°C.

The reaction of $Ni(COD)_2$ with L can be thought of as occurring in three stages, represented by eq. 2—4.

$$Ni(COD)_2 + 2\,L + \Delta H_2 \rightarrow (COD)NiL_2 + COD \qquad (2)$$

$$(COD)NiL_2 + L + \Delta H_3 \rightarrow NiL_3 + COD \qquad (3)$$

$$NiL_3 + L + \Delta H_4 \rightarrow NiL_4 \qquad (4)$$

In most cases only $\Delta H_2 + \Delta H_3 + \Delta H_4$ can be determined. This is the value shown in Table 1 when the product is NiL_4. $P(OMe)_3$ and $PPhMe_2$ are typical cases in Fig. 1; an endpoint in the calorimetric titration occurs at a 4:1 ratio of L/Ni.

With large ligands, reaction stops with eq. 2 or 3. One such example is $Ni(PPh_3)_3$. Failure to form a $Ni(PPh_3)_4$ complex is consistent with earlier molecular weight [2] and UV studies [3] which show no association in solution to form a NiL_4 complex, and supports the idea [3] that the solid with the composition $Ni(PPh_3)_4$ is more properly written as $Ni(PPh_3)\cdot PPh_3$ [15].

The known heat of vaporization of metallic nickel (H_5 = 101.6 kcal/mol) [4] can be used to determine mean Ni—P bond energies, defined by eq. 6 and 7. The

$$Ni(s) \rightarrow Ni(g, 25°C) \qquad (5)$$

$$\text{For } NiL_4\text{:} \quad 4\,D(Ni\text{—}P) = \Delta H_5 + \Delta H_1 - (\Delta H_2 + \Delta H_3 + \Delta H_4) \qquad (6)$$

$$\text{For } NiL_3\text{:} \quad 3\,D(Ni\text{—}P) = \Delta H_5 + \Delta H_1 - (\Delta H_2 + \Delta H_3) \qquad (7)$$

mean D(Ni—olefin) in $Ni(COD)_2$ is clearly 1/4 (101.6 − 3) = 24.6 kcal/mol. Assuming the same value in $(COD)NiL_2$ complexes, we can calculate D(Ni—P) by eq. 8.

$$\text{For } (COD)NiL_2\text{: } 2\,D(Ni\text{—}P) + 2\,D(Ni\text{—olefin}) = \Delta H_5 + \Delta H_1 - \Delta H_2 \qquad (8)$$

Comparison of our values (Table 1) with $D(Ni\text{—}PF_3)$ = 35.2 ± 0.8 kcal/mol in

TABLE 1

ENTHALPIES FOR THE REACTION OF EXCESS L WITH $Ni(COD)_2$ IN TOLUENE AT 25°C

Ligand	θ^a (°)	$-\Delta H^b$ (kcal/mol)	Product^c	D(Ni—P)^d (kcal/mol)	Strain^e in NiL (kcal/mol)
$PPh(OEt)_2$	116	57	NiL_4	39.0	−6
$P(OMe)_3$	107	51	NiL_4	37.5	(0)
$P(OEt)_3$, $P(OCH_2CH_2Cl)_3$	109	48	NiL_4	36.8	3
PPh_2OMe	132	46	NiL_4	36.2	5
P(O-i-Pr)$_3$	130	44	NiL_4	35.8	7
$P(OPh)_3$	128	39^f	NiL_4	34.5	12
$PPhMe_2$, t-BuNC	122^g	38	NiL_4	34.2	13
PMe_3, P(*O*-*p*-tolyl)$_3$	118, 128	36	NiL_4	33.7	15
PPh_2Me	136	32	NiL_4	32.8	19
P(*O*-*o*-tolyl)$_3$	141	20^f	(COD)NiL_2	34.5	18^h
PEt_3, PBu_3	132	17	NiL_3	38.6	
$PPhEt_2$	136	15	NiL_3	38.0	
P(*O*-*o*-C_6H_4-i-Pr)$_3$	148	15	(COD)NiL_2	32.0	
PPh_3	145	8^f	NiL_3	35.6	$>33^i$
P(i-Pr)$_3$, P(O-t-Bu)$_3$, P(*O*-*o*-C_6H_4-t-Bu)$_3$	160, 172, 175	0	None		

[a] Cone angle, from ref. 1. [b] The uncertainty is generally ±1 kcal/mol. [c] Determined from the end point of the calorimetric titration. [d] The mean Ni—P bond energy, defined in the text. [e] Strain = $51 + \Delta H_2 + \Delta H_3 + \Delta H_4$. [f] Added as an 0.8 *M* solution from a jacketed syringe thermostatted at 25°C. [g] For $PPhMe_2$. [h] Calculated using $\Delta H_4 = -16$ kcal/mol, from ref. 13. [i] Calculated on the basis that ΔH_4 must be less negative than −10 kcal/mol., or $Ni(PPh_3)_4$ would have been observed in ref. 3.

$Ni(PF_3)_4$ reported by Connor and coworkers [5] shows that D(Ni—P) is not strongly dependent on the electron donor—acceptor character [6] of the phosphorus ligand. t-BuNC is only slightly weaker as a ligand for nickel(0) than CO; D(Ni—CO) in $Ni(CO)_4$ is 35.1 ± 3 kcal/mol [5].

The decreasing exothermicity in the formation of NiL_4 complexes on descending Table 1 corresponds closely to the decreasing ability of the ligands to compete with each other for coordination sites on nickel(0) [7], and is obviously largely due to increased steric strain energy in complexes with bulkier L. If we neglect electronic effects and take $Ni[P(OMe)_3]_4$ as representative of a completely unstrained structure, we can obtain* the strain energies shown in the last column of Table 1. The strain energies generally increase with θ, as expected; however, for reasons which are not clear, $PPh(OEt)_2$** and PPh_2OMe give NiL_4 complexes which are less strained than would be expected from their cone angles. The smaller $-(\Delta H_2 + \Delta H_3)$ for PPh_3 (8 kcal/mol) than for PEt_3 (17) suggests that $Ni(PPh_3)_3$ may already have as much as 9 kcal/mol of strain. $Ni(PPh_3)_4$ would have more than 33.

The largest ligands ($\theta \geqslant 160°$) fail to displace any COD. It is noteworthy that ML_2 complexes with very large L have been recently isolated and structurally characterized by X-rays: $Pd[PPh(t\text{-}Bu)_2]_2$ [9, 10], $Pd(PCy_3)_2$ [10] and $Pt(PCy_3)_2$ [11].

Free energy changes can be obtained from our data if entropy changes can be estimated. For example, for the formation of NiL_4 from metallic nickel (eq. 9),

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* The procedure is much like that Brown [8] used in estimating strain energies in amine—borane complexes.

** $PPh(OEt)_2$ also did exceptionally well in the ligand competition experiments [7].

$$\text{Ni(s)} + 4\,\text{L(solution)} \rightarrow \text{NiL}_4\,\text{(solution)} \qquad (9)$$

we can estimate $\Delta S_9 \sim -4(38) + 44 = -108$ eu*. 38 eu is the mean ΔS for dissociation of an L from NiL_4 for a series of complexes [13]; 44 is the entropy change for vaporization of Ni(s) by eq. 5 [4]. Then for $Ni[P(OMe)_3]_4$ at 25°C $\Delta G_9 \sim -51 - (-3) - 0.298(-108) = -16$ kcal/mol. On this basis, one ought to be able to prepare $Ni[P(OMe)_3]_4$ from metallic Ni and the ligand.($Ni(PMeCl_2)_4$ was reported by Quin [14]); NiL_4 complexes with strain energies in excess of about 16 kcal/mol should be thermodynamically unstable with respect to decomposition to metallic nickel and free L.

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15 Dr. R.A. Schunn of our Laboratory has recrystallized "$Ni(PPh_3)_4$" and obtained crystals with a good analysis for $Ni(PPh_3)_3$.

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*For the reaction $Ni(s) + 4\,CO(g) - Ni(CO)_4\,(g)$ at 25°C, $\Delta S = -100$ eu [12].