centration is 1 *M*. Ethylene formation is also suppressed at high water concentrations. Remarkably, however, *added acetic acid or phenols*[10] *(1 M) have little effect upon this ratio.*[11] Furthermore, ethylene formation from the Hoffman elimination upon the supporting electrolyte (0.1 *M*) is not quenched by added phenols. Thus in this system tetraethylammonium ion is a more efficient proton donor toward anionic intermediates in the reduction of **1**, **2**, or **3** than are phenols, even when the latter are in tenfold excess! These results clearly imply that phenols and acetic acid are not incorporated into the inner layer[12,13] at the interface between the mercury electrode and the solution, since it is in this region that the carbanion is formed and is reacting. Added water or methanol can, however, be incorporated into this region. The surface concentration of water is lower than its concentration in bulk solution (or in the diffuse[12] part of the double layer). This is demonstrated both by electrocapillary data[14] and by our observation that generation of **6** by reaction between **1** and electrochemically generated naphthalenide ion in DMF containing 50 m*M* water affords a 60:40 mixture of **5** and **4**, while this ratio is 48:52 in the direct electrolysis of **1** in DMF containing 50 m*M* water. The decreased surface concentration of water relative to bulk solution is no doubt due in part to preferential adsorption of both tetraethylammonium ion (R_4N^+) and DMF, this adsorption having the effect of "squeezing out" water from the inner layer.[12,14] We have tested this hypothesis by changing the electrolyte to triethylammonium bromide ($R_3NH^+Br^-$). We expected by this artifice to incorporate a much stronger acid into the double layer. This expectation was confirmed: the ratio of **5** to **4** was changed from 38:62 to 92:8 with the change in electrolyte. The synthetic implications of this experiment are obvious.

Much more work will be necessary before these effects are understood. The significance for electrochemical investigations is clear, however; it is often supposed that phenol and carboxylic acids are efficient proton donors toward anions in DMF, and conversely, that failure to quench an electrochemical reaction by addition of one of these implies that it does not involve carbanionic intermediates. While these conclusions may often be justified, our results imply that neither need necessarily be true.[15]

Acknowledgment. This work was supported by the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation. The Electrochemical Society awarded a Colin Garfield Fink summer fellowship to R. G. R. Experimental conditions for the water analysis by vpc were worked out by Mr. Richard C. Reed and Mr. Walter Morgan. Professor Harry B. Mark made a number of valuable comments upon the manuscript.

Albert J. Fry,* Roberta G. Reed
Hall-Atwater Laboratories of Chemistry
Wesleyan University, Middletown, Connecticut 06457

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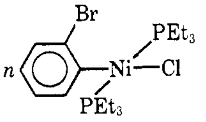
Synthesis of a Nickel Heterocycle

Sir:

We wish to report a new type of transformation in organo–transition metal chemistry. Treatment of diethyl ether solutions of *trans*-chloro(2-bromophenyl)-bis(triethylphosphine)nickel(II)[1] (**1**) with lithium metal at −40 to −78° has afforded essentially quantitative yields of lithium bromide, lithium chloride, and of an organonickel compound, **2**, derived from removal of the halogen elements from **1**. Compound **2** is a bright yellow crystalline solid at room temperature and is extremely air sensitive. All experiments were therefore conducted with the rigorous exclusion of atmospheric oxygen and moisture by using standard vacuum-line techniques. The compound slowly decomposes at room temperature, but it can be stored for months *in vacuo* at −78° and its solutions are stable for hours at 0°.

The progress of the reaction of **1** with lithium was monitored by following the change in the aromatic pmr spectrum with time. The unsymmetrical spectrum of **1** was gradually converted to a symmetrical AA′BB′ spectrum, and no pmr evidence for an intermediate species was obtained. The chemical change only occurred when lithium metal was present.

The stoichiometry, as indicated by eq 1, was demonstrated in the following manner. Compound **1** was treated with an accurately measured moderate excess of



1

$$+ \ 2n\mathrm{Li} \longrightarrow$$

$$[\mathrm{C_6H_4Ni(PEt_3)_2}]_n + n\mathrm{LiCl} + n\mathrm{LiBr} \quad (1)$$

2

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(10) Phenol, hydroquinone, and 2,4,5-trimethylphenol were all tried.

(11) A slight decrease in the relative proportion of **4** is observed in the presence of 1 *M* phenols, if $[H_2O] < 100$ m*M*, but this effect is much less than that produced by addition of 1 *M* water. Similar results are observed for acetic acid where $[H_2O] < 350$ m*M*.

(12) D. M. Mohilner, *Electroanal. Chem.*, **1**, 241 (1966).

(13) Electrocapillary curves show that phenol and resorcinol are not specifically adsorbed on the mercury surface in DMF: J. Janata, J. Gendell, R. G. Lawton, and H. B. Mark, Jr., *J. Amer. Chem. Soc.*, **90**, 5226 (1968), footnote 15.

(14) R. Payne, *Advan. Electrochem. Electrochem. Eng.*, 7, 1 (1970).

(15) Dihalides **1**–**3** have polarographic half-wave potentials of −1.54, −0.93, and −0.83 V, respectively, relative to the reference electrode of Marple.[16] Preparative electrolyses were carried out at controlled potential, at *ca.* −1.8 V for **1** and −1.1 V for **2** and **3**. These potentials are considerably cathodic of the electrocapillary maximum, which is at *ca.* 0 V in this system, as determined by electrocapillary measurements.

(16) L. W. Marple, *Anal. Chem.*, **39**, 844 (1967). This electrode is *ca.* −0.7 V relative to sce.

(1) Treatment of *trans*-dibromobis(triethylphosphine)nickel(II) with 2-bromophenylmagnesium bromide in diethyl ether[2] or oxidative addition of *o*-dibromobenzene to ethylenebis(triethylphosphine)nickel-(0) afforded **1**, mp 105.1–105.3°, after chromatography of the product on Baker aluminum oxide Analytical Reagent for Chromatography, pH 3.8. Bromide bonded to nickel in the primary product was quantitatively replaced by chloride on the alumina column. The general experimental procedure used in the oxidative-addition reaction was essentially the same as that described for the synthesis of *trans*-chloro(trichlorovinyl)bis(triethylphosphine)nickel(II),[3] with the exception that a longer reaction time was employed. This procedure afforded a 52% yield of **1**. The extension of this method to the preparation of arylnickel compounds was first demonstrated by Fahey.[4]

Satisfactory analyses were obtained for **1** and for iodo compound **3** which is described in the text.

(2) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).

(3) (a) R. G. Miller, D. R. Fahey, and D. P. Kuhlman, *J. Amer. Chem. Soc.*, **90**, 6248 (1968); (b) R. G. Miller, R. D. Stauffer, D. R. Fahey, and D. R. Parnell, *ibid.*, **92**, 1511 (1970).

(4) D. R. Fahey, *ibid.*, **92**, 402 (1970).

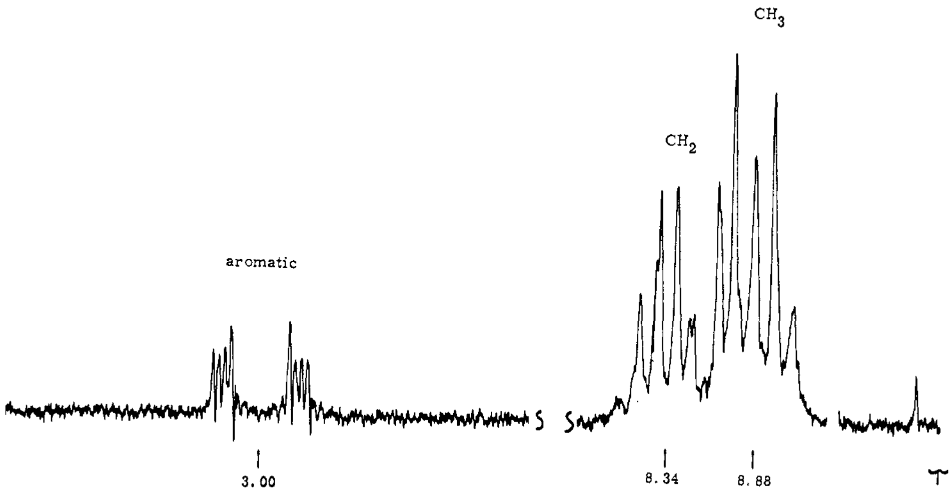


Figure 1. The 60-MHz pmr spectrum of **2** recorded at 40° in tetrachloroethylene solution. Chemical shifts are reported relative to tetramethylsilane. The spectra of **2** in deuterioacetone and dimethyl ether, recorded at 0°, were very similar to this spectrum.

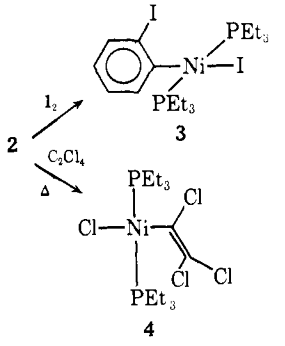
lithium and the reaction was allowed to proceed until the formation of **2** was complete as evidenced by pmr monitoring. The resultant diethyl ether solution containing **2** and the lithium halides was then carefully separated from unreacted lithium metal. The mole ratio of lithium consumed:**1** employed was found to be 1.90 by titration of lithium hydroxide derived from hydrolysis of excess lithium, and 1.93 by the volume of evolved hydrogen. These values correspond to a 95–96.5% conversion of **1** to **2** if a Li:Ni ratio of 2.0:1.0 were required. The lithium halides were quantitatively separated from **2** by removal of the ether solvent and extraction of the residue with hexane. Total halogen in the lithium halide mixture was determined gravimetrically as silver halide. The value obtained was 95% of that expected for the formation of 1 mol each of LiCl and LiBr from each mole of **1** employed.

The aromatic pmr spectrum (60 MHz) of **2** at 0° was essentially identical in diethyl ether, deuterioacetone, deuteriobenzene, hexane, dimethyl ether, and tetrachloroethylene. The chemical shift between the A and B components of the spectrum exhibited a small solvent dependence, but the line separations and relative peak intensities in each multiplet were solvent insensitive. Integration of the peak areas of the aromatic and alkyl proton resonances indicated a $Et_3P:C_6H_4$ ratio of 2:1.

The spectrum of **2** recorded at 40° in tetrachloroethylene (Figure 1) was identical with those obtained at lower temperatures in the same solvent. The compound rapidly decomposed above room temperature in diethyl ether and deuterioacetone.

Treatment of a hexane solution of **2** with iodine at 0° (I_2:Ni = 0.76:1.00) afforded *trans*-iodo(2-iodophenyl)bis(triethylphosphine)nickel(II) (**3**) in 67% yield based on the limiting reagent (I_2), and 51% based on moles of nickel employed. Thermolysis of **2** at 92–96° in tetrachloroethylene afforded a 36% yield of *trans*-chloro(trichlorovinyl)bis(triethylphosphine)nickel(II)[3] (**4**) and hydrocarbon material, largely polymeric, which has not been characterized.

These results indicate that **2** possesses an empirical formulation of $(C_6H_4)Ni(PEt_3)_2$, the aromatic ligand existing as a symmetrically ortho-disubstituted benzene. The very facile formation of **3** on reaction of **2** with iodine precludes a complex derived from $(Et_3P)_2Ni$ and a cyclic polyarene as a reasonable structural candidate. We feel that two structural possibilities remain which meet the symmetry requirements imposed by the spectral data and which satisfy the established stoichiometry and chemical evidence: (1) a monomeric formulation in which the C_6H_4 unit is bound directly to one metal atom, and (2) a structure in which each C_6H_4 unit is bonded simultaneously to two metal atoms.



In an attempt to distinguish between these two cases, the molecular weight of a twice-recrystallized sample was determined by vapor-pressure lowering of *n*-butane at 0°. It was found that the apparent molecular weight was extremely concentration dependent, suggesting a dissociating system. Accordingly, a complete concentration dependence of the molecular weight was undertaken in order to establish the limiting apparent molecular weight at infinite dilution.[5]

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(5) The apparatus used for the measurements allowed direct reading of the vapor-pressure lowering across a differential mercury manometer referenced to pure butane samples. Much difficulty was encountered in early experiments when very dilute solutions were employed; anomalously high molecular weights were obtained. This effect has been reported by others; see D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, p 71, and references therein. The difficulty was found to originate in two principal systematic errors which led to nonzero null readings when only butane was present in each arm of the apparatus.

Nearly zero null readings (±0.02 mm) were obtained when the quantities of butane in each arm were very closely matched and when the vapor-phase volumes of the two sides were nearly identical. The differences which otherwise were found must have originated in a fractionation effect, even though Phillips research grade butane of 99.97 mol % purity was used.

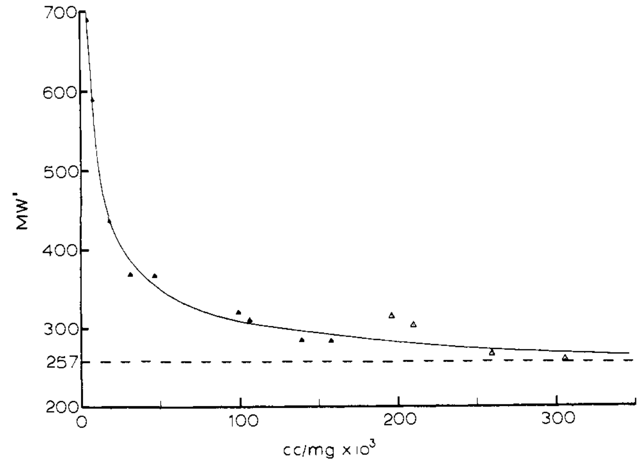
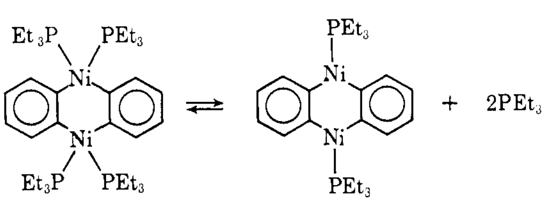


Figure 2. The concentration dependence of the apparent molecular weight (MW′) of **2** in *n*-butane at 0°.

Figure 2 shows a plot of the observed molecular weight *vs.* the reciprocal of the concentration. The nine most dilute points were used to calculate a least-squares linear regression equation which is plotted as a solid line and which gives an intercept at infinite dilution of 257 amu (dotted line). The standard deviation of the intercept was ±9 amu, allowing limits of 232–282 to be imposed at a 95% confidence level. These data are not compatible with a monomeric formulation for **2**, since its dissociation should give either a two- or three-particle system at infinite dilution and limiting molecular weights of 185 and 124, respectively. On the other hand, they are in good agreement with the alternative cyclic dimer structure,[6] which would give a limiting molecular weight of 247 as a three-particle system (eq 2).



(2)

Evidence for this type of dissociation was found in the pmr spectrum of **2**. The triethylphosphine CH_3 protons do not appear to be coupled to the phosphorus nucleus in an adjacent ligand. The characteristic virtual coupling of CH_3 protons to phosphorus nuclei in nondissociating planar bis(triethylphosphine)–group VIII metal complexes has served as a basis for configurational assignments.[3,7] Addition of triethylphosphine to a solution of **2** in dimethyl ether (excess Et_3P:Ni = 2:1) caused essentially no change in the fine structure or in the chemical shifts of the aromatic proton resonances or of the Et_3P ligand methyl resonances. The P-CH_2 resonance increased in complexity and was shifted *ca.* 13 Hz to high field relative to its position in the spectrum of **2**. The spectrum of triethylphosphine in dimethyl ether is very different from that of the Et_3P ligands in **2**, yet no "free" triethylphosphine could be detected in the mixture. The results suggest that the Et_3P ligands are exchanging rapidly on the pmr time scale.

The near quantitative yield of **2** poses intriguing questions concerning the mechanism by which it is formed. Further studies of this and related organotransition metal systems are in progress.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the University of North Dakota grant-in-aid program for support of this research.

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(6) Molecular models indicate that the dimer, 9,10-di[bis(triethylphosphine)nickelo]-9,10-dihydroanthracene, should not exist as a planar molecule. If the nickel bonding systems possess cis-planar configurations, the planes of the benzene rings lie substantially outside of the nickel bonding planes and the heterocyclic ring should be frozen in a pseudoboat conformation. The rather severe steric requirements of the Et_3P ligands in the cis-planar configuration could account for the very pronounced tendency of the molecule to dissociate in solution. We were unable to construct an analogous model of the hypothetical cyclic trimer. The steric restrictions are so severe that each nickel atom can accommodate only one Et_3P ligand.

(7) (a) G. W. Parshall, *J. Amer. Chem. Soc.*, **88**, 704 (1966); (b) H. C. Clark and W. S. Tsang, *ibid.*, **89**, 533 (1967); (c) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc., London*, 279 (1963).

(8) National Science Foundation Predoctoral Fellow, 1969–1970.

Jerry E. Dobson,* Roy G. Miller,* James P. Wiggen[8]
Department of Chemistry, University of North Dakota
Grand Forks, North Dakota 58201

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Application of Solvent Effects to the Study of Diamagnetic and Paramagnetic Ring Currents

Sir:

Because of their diamagnetic ring currents and specific solvent–solute interactions, aromatic solvents induce strong shifts in the proton nmr spectra of dipolar molecules.[1] In the present communication we suggest that specific solvent effects in potentially homoaromatic and antiaromatic solvents can provide valuable information about molecular magnetic anisotropies.

The chemical shift difference between acetonitrile and cyclohexane (internal reference) in a solvent X is $\Delta\sigma_X = \Delta\sigma_{gas} + \Delta\sigma_{medium}$. Referring all $\Delta\sigma_X$ values to $\Delta\sigma_{cyclohexane}$ (the observed chemical shift difference between acetonitrile and cyclohexane in neat cyclohexane), the relative solvent shifts $\Delta\sigma_X - \Delta\sigma_{cyclohexane}$ (for brevity, *S*) are isolated. For benzenoid hydrocarbons, *S* values are very large owing to a specific anisotropy effect: the positive end of the acetonitrile dipole is preferentially located above the plane of the ring where π-electron density and diamagnetic shielding are greatest.[2] This specific anisotropy effect is very much larger than the reaction field and van der Waals and nonspecific anisotropy terms, and will outweigh these even in only moderately anisotropic hydrocarbon solvents. *S* values should therefore be a direct measure of the magnetic anisotropy experienced in the time-averaged complex, if acetonitrile were associated with all hydrocarbons to the same extent. In practice, the association constants differ but are sufficiently similar to make *S* a valuable qualitative measure for the anisotropy experienced.[3]

The *S* values of "normal" olefins are close to zero (Figure 1).[4,5] The *S* value of benzene, on the other

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(1) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960); (b) P. Laszlo, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 231 (1967); (d) J. Ronayne and D. H. Williams, *Annu. Rev. NMR Spectrosc.*, **2**, 83 (1969).

(2) W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).

(3) The determination of association constants and limiting solvent shifts for the quantitative study of some systems of interest is currently in progress.