positioned on geometric grounds (C–H 0.95 Å) and an overall hydrogen atom thermal parameter refined to a value of 0.0687 (3) Å^2. Crystal data, data collection, and least-squares parameters are listed in Table II. An ORTEP[20] diagram of the structure is given in Figure 2.

Acknowledgment. This research was supported by the National Research Council of Canada. A.B. is grateful to the Austrian Trade Commission for a grant in support of his study visit to Canada.

Registry No. **10a**, 18549-83-2; **10b**, 79184-72-8; **12**, 136804-43-8; **13**, 136804-44-9; **18**, 136804-45-0; **19**, 136804-46-1; **20**, 136804-47-2; **21**, 136804-48-3; $\mathbf{21}\cdot{}^1/_2C_6D_6$, 136804-49-4; **22**, 136804-50-7; **23**, 136804-51-8; **26**, 136804-52-9; **27**, 136804-53-0; **28**, 84966-07-4; **30**, 136804-54-1; AdCOCl, 2094-72-6; MeOH, 67-56-1.

Supplementary Material Available: For **21** and **26**, tables of atomic coordinates, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, torsion angles, and least-squares planes (20 pages); listings of observed and calculated structure factors for compounds **21** and **26** (34 pages). Ordering information is given on any current masthead page.

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Synthesis and Fluxional Behavior of [Bis(trialkylphosphine)nickelio]anthracene (Alkyl = Et, Bu)[1]

Amnon Stanger*[2a] and K. Peter C. Vollhardt*[2b]

Department of Chemistry, University of California at Berkeley, and Chemical Sciences Division,
Lawrence Berkeley Laboratory, Berkeley, California 94720, and Department of Chemistry,
Technion—Israel Institute of Technology, Haifa 32000, Israel

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The title compounds were prepared from the respective $(R_3P)_2NiCl_2$ complexes and magnesium–anthracene–$(THF)_3$ (or anthracene in the presence of Mg or C_8K). The assignment of the anthracene proton NMR signals using NOE in conjunction with magnetization-transfer techniques is described. The complexes undergo haptotropic rearrangements in which the $(R_3P)_2Ni$ moiety migrates between the two terminal rings of the coordinated anthracene. The rates of these processes are concentration independent and unaffected by the presence of free anthracene and tris(trialkylphosphine)nickel. Kinetic studies in the temperature range –60 to +70 °C using line shape analysis and spin saturation transfer techniques were carried out. It was found that $\Delta H^{\ddagger} = 13.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -4.3$ eu for the haptotropic rearrangement in **2**, and similar values were found for **1**. Possible mechanisms are discussed. According to ^1H, ^{13}C, and ^{31}P NMR data, the coordination number between the anthracene and the $(R_3P)_2Ni$ moiety is 4. However, an equilibrium between two η^2 structures with $\Delta G^{\ddagger} \leq 4$ kcal mol^{-1} cannot be ruled out.

Introduction

The fluxional behavior of numerous transition-metal arene complexes has been investigated.[3] However, not many such species containing anthracene are known, and very few have been studied with respect to their dynamic properties.[4] It is of general interest to investigate the dynamic, structural, and chemical behavior of these complexes because of the haptotropic rearrangements they may undergo, processes that are isolobal to some sigmatropic rearrangements in organic chemistry. The haptotropic rearrangement of a metal fragment on polyaromatic systems could also be viewed as a soluble model for a metallic moiety migrating on a surface. Thus, these studies have potential interest for the understanding of surface chemistry.

Ni(0)–anthracene complexes exhibit in addition two main unique features. The first arises from the possibility of nickel to form stable 16e and 18e complexes. The stable electronic configuration of such a complex is probably ligand dependent. For example, $(R_3P)_2Ni(olefin)$ is more stable than $(R_3P)_2Ni(olefin)_2$ [although η^4-butadiene–Ni$(PR_3)_2$ has been prepared[5]] but $Ni(CO)_3$ is far less stable than $Ni(CO)_4$. [Bis(trialkylphosphine)nickelio]anthracene can probably adopt both coordination numbers, depending

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[1] Presented in part at the Fourth International Conference on The Chemistry of Platinum Group Metals, University of Cambridge, Cambridge, U.K., July 9–13, 1990.

[2] (a) Technion. (b) University of California at Berkeley.

[3] (a) Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, D. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1977**, *99*, 5518. (b) Zigler, T. *Inorg. Chem.* **1985**, *24*, 1547. (c) Ann, B. E. *Chem. Soc. Rev.* **1986**, *15*, 167. (d) Hu, X.; Duchowski, J.; Pomeroy, R. K. *J. Chem. Soc., Chem. Commun.* **1988**, 362. (e) Ustynyuk, N. A. *J. Organomet. Chem.* **1984**, *270*, 185. (f) Pomeroy, R. K.; Harrison, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 661. (g) McGlinchey, M. J.; Fletcher, J. L.; Sayer, B. G.; Bougeard, P.; Faggiani, R.; Lock, C. J.; Bain, A. D.; Rodger, C.; Kunding, E. P.; Astruc, D.; Hamou, J. R.; Le Maux, P.; Top, S.; Jaouen, G. *J. Chem. Soc., Chem. Commun.* **1983**, 634. (h) McGlinchey, M. J.; Bougeard, P.; Sayer, B. G.; Hafner, R.; Lock, C. J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 789. (i) Hunter, G.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1984**, 172. (j) Iverson, D. J.; Hunter, G.; Blount, J. F.; Danewoof, J. R.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073. (k) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 31. (l) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (m) Hofmann, P.; Albright, T. A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 728. (n) Campi, E. M.; Gatehouse, B. M. K.; Jackson, W. R.; Rae, I. D.; Wong, M. G. *J. Chem. Soc., Chem. Commun.* **1984**, 175.

[4] To the best of our knowledge, the only transition-metal anthracene complex studied for its fluxional behavior is $(dmpe)_2(Cl)Ta$–anthracene, revealing rotations around the metal arene bond. Bianconi, P. A.; Williams, I. D.; Lippard, S. J. Submitted for publication. We are grateful to professor Lippard for sending us the data prior to publication.

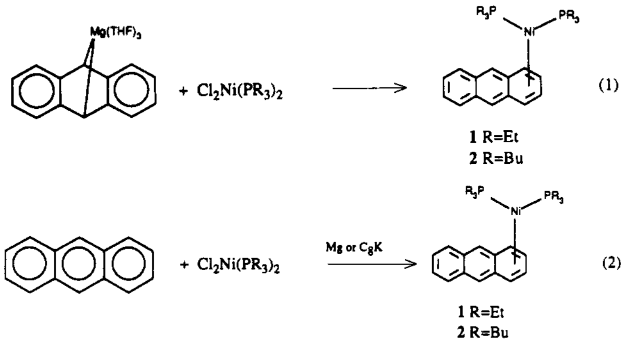
[5] Albright, T. A.; Krüger, C. Personal communication.

on the phosphines. Thus, when the phosphine's alkyls are cyclohexyls, the Ni moiety is bound η^2 to the anthracene,[6] whereas the respective bonding in the title complexes is probably η^4 (see below). This property opens up the possibility to study the coordination number change between a metal and a ligand as a function of the other ligands, a process which is thought to be a key step in many catalytic reactions. For example, when the ligand is ($Et_2P-CH_2-CH_2-PEt_2$) an equilibrium between two η^2 structures is observed at low temperatures.[7] A second interesting property of these complexes is the unimolecular rearrangement they undergo,[8] in which the $(R_3P)_2Ni$ moiety migrates from one terminus to the other of the ligand. Synthetically, these complexes may also function as convenient and reactive sources of $(R_3P)_2Ni$.[9]

We wish to report here the preparation and detailed dynamic study of two parent members of the Ni–anthracene family of complexes.

Results and Discussion

The complexes 1 and 2 are obtained from the reaction of magnesium–anthracene with the respective Ni(II) complex (eq 1) or via reductive olefination using metallic magnesium or C_8K[10] as the reducing agents (eq 2). The NMR data are in full agreement with the assigned structure. At low temperature ($T < 243$ K, 300-MHz spectrometer) the ^{31}P spectra show two doublets (an AB pattern) which are ca. 8 and 12 ppm apart for 1 and 2, respectively, indicating a rather different magnetic environment for each phosphine. These spectra are in accordance with a pseudotetrahedral geometry around the nickel, which causes one phosphine to be on top of the naphthalene residue, whereas the other phosphine points outside. The proton spectra consist of two AA′BB′ patterns, one for the complexed (H_1–H_4), one for the uncomplexed ring protons (H_5–H_8), and a singlet for H_9 and H_{10}. The phosphine alkyls resonate at higher field (0.5–1.7 ppm) with complicated splitting due to phosphorus couplings. An η^2 complex is expected to give a totally different splitting pattern (i.e., ABCD instead of AA′BB′) and probably a smaller chemical shift diffence between the two ^{31}P resonances. Cooling the sample to −100 °C does not change the appearance of the spectra, including the absence of line broadening. These data are in accordance with the presence of a pseudotetrahedral 18e nickel center which is coordinated η^4 to the anthracene. However, an equilibrium between two η^2 structures with a $\Delta G^\ddagger \leq 4$ kcal mol^{-1} cannot be ruled out.[11]



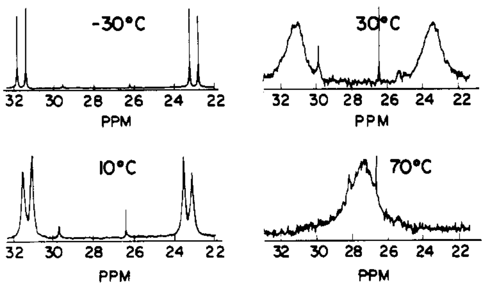


Figure 1. ^{31}P VTNMR spectra of 2. Chemical shifts are uncalibrated.

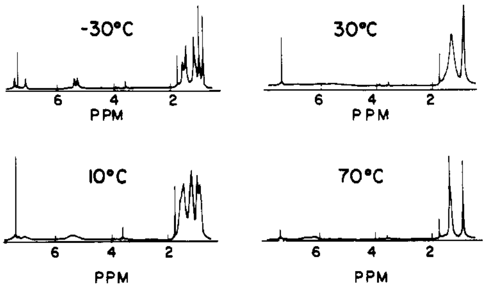


Figure 2. ^1H VTNMR spectra of 2.

The assignment of the anthracene protons in 1 and 2 is supported by NOE in conjunction with spin saturation transfer experiments. Irradiation of the low-field part of the AA′BB′ pattern associated with the complexed ring protons at −60 °C results in NOE enhancement of the H_9 and H_{10} signal and a decrease of the low-field part of the AA′BB′ belonging to the uncomplexed ring protons due to saturation transfer. Irradiation of the high-field part of the AA′BB′ pattern associated with the complexed ring protons results in the decrease of the respective part in the uncomplexed site only. These data allow the assignment of the low-field part of the two AA′BB′ patterns being due to H_1 and H_4 at the complexed site and H_5 and H_8 at the uncomplexed site. The other parts of the two AA′BB′ patterns were thus assigned as H_2, H_3 and H_6, H_7, respectively.

When an NMR sample of 1 and 2 in THF-d_8 is warmed above −30 °C (300 MHz), coalescence is observed. The two ^{31}P doublets merge to form a singlet at the high temperature limit (Figure 1), indicating the equilibration of the two initially different phosphines. More than one possible process could account for these observations, for example, rotation around the Ni–anthracene bond, ring whizzing, haptotropic rearrangement across the anthracene, etc.

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(6) Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1977**, *16*, 884.

(7) Stanger, A. Unpublished results.

(8) Stanger, A. *Organometallics* **1991**, *10*, 2979.

(9) Shazar, A.; Stanger, A. *Unpublished* results.

(10) C_8K is prepared by heating the respective amounts of potassium and graphite until bronze-colored powder is obtained. For a recent review see: Csuk, R.; Glänzer, B. I.; Fürstner, A. *Adv. Organomet. Chem.* **1988**, *28*, 85.

(11) Recently, a detailed dynamic study of a similar naphthalene complex was published. Benn, R.; Mynott, R.; Topolović, I.; Scott, F. *Organometallics* **1989**, *8*, 2299. See also: Scott, F.; Krüger, C.; Betz, P. *J. Organomet. Chem.* **1990**, *387*, 113. The authors compare solid and solution NMR data for the complexes and conclude that a low barrier exists for the equilibrium between two η^2 isomers (which can be observed in the solid state) and that the rearrangement across the naphthalene (which is observed in solution) has a higher barrier. However, there are some important differences between their systems and ours. The arene is naphthalene and not anthracene and the phosphines are bulky and bridged, a fact which might be important regarding the Ni–anthracene bonding. Thus, the cone angle of Bu_3P and Et_3P is 132° whereas the respective angle in $(Cy)_3P$ is 170° (Tolman, A. C. *Chem. Rev.* **1977**, *77*, 313). Therefore, the electronic properties of the $(R_3P)_2Ni$ moiety depends strongly on the type of phosphine ligands, and thus different phosphines can cause different bonding to the aromatic ligand. Another important difference between the systems is that the authors observed line broadening of the solution sample at −100 °C, which we do not. Thus, these results (and those which are presented in ref 6) do not necessarily mean that 1 and 2 are also η^2 complexes.

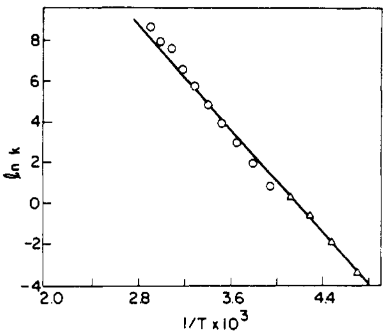
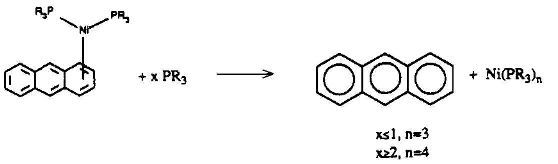


Figure 3. Plot of ln k vs $1/T$ for the kinetic data of 1: (△) obtained from spin saturation transfer; (○) obtained from line shape analysis.

However, the proton spectra are in accordance only with haptotropic rearrangement across the anthracene. Thus, as the sample is warmed, the signals attributed to H_1–H_4 and H_5–H_8 coalesce to a new (unresolved) AA′BB′ pattern at the average chemical shift of the initially different two groups of signals (Figure 2). During this process the singlet attributed to H_9 and H_{10} stays virtually unchanged. Thus, the dynamic process observed equilibrates $H_{1,4}$ with $H_{5,8}$, and $H_{2,3}$ with $H_{6,7}$, and therefore, at the high-temperature limit, both sides of the anthracene are equal on the NMR time scale. The only explanation for these observations is rapid migration of the $(R_3P)_2Ni$ moiety between the two ends of the bound anthracene.

In order to shed some light on the mechanism of the process, we carried out some studies regarding the rates of the processes. First, it was found that the rate is concentration independent within a concentration range of 0.012–0.2 M.

Second, we attempted to measure the rates in the presence of phosphines. However, 1 and 2 react with free phosphine, even at very low temperature,[12] to yield free anthracene and tris- or tetrakis(trialkylphosphine)nickel, depending on the amount of the phosphine introduced (eq 3). Introduction of 0.5 equiv of Bu_3P to an NMR sample of 2 decomposes half of the starting complex. The remaining $(Bu_3P)_2Ni$–anthracene shows the same VT spectra as clean 2; i.e., the rearrangement rate is unaffected by the presence of free anthracene and tris(tributylphosphine)nickel. These data suggest that the rate-determining step of this rearrangement is unimolecular.



(3)

The rates of the rearrangements were then studied at a temperature range of −60 to +70 °C. Spin saturation transfer techniques[13] for the ¹H spectra were used for the lower temperature range (−70 to −30 °C), and line shape analysis[14] was used for the ³¹P spectra at the higher temperature range. Figure 3 shows the plot of log k as a function of $1/T$. Note that the points obtained from the ³¹P data from the line shape analysis form the same straight line as the ¹H data obtained from spin saturation transfer measurements. Thus, the same process is monitored by the ¹H and ³¹P spectra.[15] Linear regression analysis of these data (correlation coefficient = 0.997) gives $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 13.6 kcal mol^{-1} and −4.3 eu, respectively, and the reaction parameters for 2 are similar within ±1 kcal mol^{-1} and ±2 eu. $\Delta H^{\ddagger}$ indicates that about 50% of the Ni–anthracene bond breaks at the transition state,[16] and $\Delta S^{\ddagger}$, being small, indicates that neither dissociation nor association type processes exist at the rate-determining step (otherwise a large positive or negative value, respectively, would be expected). Thus, both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ support the unimolecularity of the rate-determining step. Later studies[8] proved that the rearrangement (and not only the rate-determining step) is intramolecular.

Two possible reaction pathways might exist for the process. The first is the "least motion" mechanism, which involves the 16e Ni(II) intermediate (or transition state), similar in structure to magnesium–anthracene (Figure 4a). The second possible mechanism involves a "walk around the π system" (Figure 4b), i.e. the migration of the $(R_3P)_2Ni$ moiety via a series of η^2–η^3 changes along the system's outer CC double bonds. Orbital considerations[17] suggest that the second path is most likely since the Ni(II) intermediate (path a) suffers from strong antibonding interactions, whereas relatively not much bonding is lost on path b.[18] We are currently investigating this issue (among other mechanistic and preparative aspects of the complexes) by studying the effect of bulky substituents at the 9- and 10-positions on the rearrangement rate and extending our work to bis(trialkylphosphine)nickel–tetracene complexes. The relative rates of the rearrangement in these systems (as compared to 1 and 2) should be indicative as to the rearrangement mechanism.

Experimental Section

Starting Material and Instrumentations. All manipulations were carried out under Ar or N_2 using vacuum and Schlenk techniques. Solvents were freshly distilled prior to use: THF from potassium benzophenone ketyl and both hexane and pentane from CaH_2. THF-d_8 (the NMR solvent in all cases) was kept under vacuum over potassium benzophenone ketyl and vacuum-transferred to the NMR tube which was torch-sealed. Anthracene was recrystallized from benzene/ethanol. Magnesium–anthracene–$(THF)_3$ was prepared according to the literature.[19] All other starting materials (Strem Chemicals Inc.) were used as purchased without further purification. Elemental analyses were performed by the Berkeley Microanalysis Laboratory. NMR spectra were taken on a BVX-300 (home built) or Bruker AM-400 spectrometer. NMR chemical shifts are reported in ppm relative to TMS (¹H and ¹³C) or an external standard of H_3PO_4 in THF-d_8 (³¹P). Coupling constants are reported in hertz. IR spectra were recorded on a Perkin-Elmer 298 infrared spectrometer (hexane solution against hexane blank). Absorptions are reported in

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(12) When tributylphosphine is injected into a frozen solution of 2 in THF-d_8, the reaction takes place immediately as the solution melts, as evident from the dramatic color change (deep red to light yellow). See also: Boennemann, H.; Bogdanović, B. German Patent No. GER. Offen DE 3,205,550; *Chem. Abstr.* **1984**, *100*, 2285, Abstr. *No.* P22805b.

(13) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: 24-28 Oval Rd, London NW1 7DX, U.K., 1982; pp 53–58.

(14) The DYNAMAR program was used for spectral simulations: written by P. Z. Meakin and modified by S. T. McKenna Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720.

(15) This conclusion is true unless there is an unlikely coincidence of two different processes that are kinetically identical.

(16) (a) Tolman, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 2780. (b) Cook, C.; Wan, K. Y. *Inorg. Chem.* 1971, *10*, 2696. (c) Sakaki, S.; Kitaura, K.; Morokuma, K.; Ohkubo, K. *Inorg. Chem.* **1983**, *22*, 104. (d) Zigler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558.

(17) Albright, T. A. Personal communication.

(18) For related studies see: (a) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396. (b) Silvestre, J.; Albright, T. A. *J. Am. Chem. Soc.* **1985**, *107*, 6829. (c) Silvestre, J.; Albright, T. A. *Nouv. J. Chim.* **1985**, *9*, 659.

(19) Ramsden, H. E. U.S. Patent 3 388 179, 1968; *Chem. Abstr.* **1968**, *69*, 67563. Best results were obtained using magnesium powder (activated by 1,2-dibromoethane) sonicated with 1.1 equiv of anthracene in THF for ca. 2 h and than stirred for an additional 24–72 h. The orange precipitate is filtered from the green solution, washed with THF until the washings are yellow, and dried on the vacuum line. The yield of the air-sensiive, pyrophoric magnesium anthracene is quantitative (≥92%).

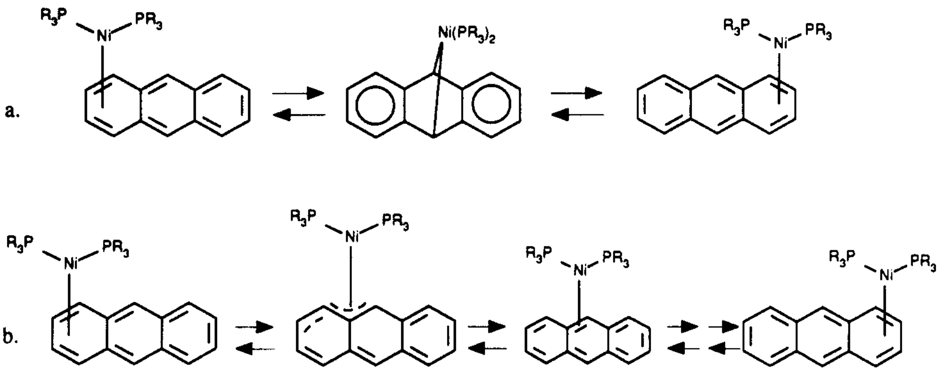

Figure 4. Possible rearrangement pathways in $(R_3P)_2Ni$–anthracene.

inverse centimeters as w (weak), m (medium), and s (strong).

$(R_3P)_2NiCl_2$. The procedure given is for the preparation of $(Bu_3P)_2NiCl_2$. It is identical with that used for $(Et_3P)_2NiCl_2$. Anhydrous $NiCl_2$ (2.902 g, 22.39 mmol) was dried on the vacuum line (1–10 mTorr, 200 °C) overnight in a Schlenk tube equipped with a reflux condenser and a magnetic stirring bar. After the flask was cooled to room temperature and filled with Ar, tributylphosphine (12.5 mL, 10.15 g, 50.17 mmol) and THF (50 mL) were added, and the reaction mixture was refluxed for 24 h. Volatiles were removed under vacuum, and the residue was dissolved in pentane (50 mL). The solution was allowed to stand for 4 days at −80 °C, and the mother liquor was cannulated from the red precipitate which formed. The precipitate was washed with cold pentane (−78 °C, 2 × 50 mL) and dried on the vacuum line. Sticky red crystals are obtained (10.76 g, 20.1 mmol, 89% yield). Anal. Calcd: C, 53.96; H, 10.19; Cl, 13.27; P, 11.59. Found: C, 54.00; H, 10.33; Cl, 13.06; P, 11.61. ^{1}H NMR (room temperature): 1.35–1.85 {m, 18 H, P–[$(CH_2)_3$–$CH_3]_3$}, 0.9–1.1 {m, 9 H, P–[$(CH_2)_3$–$CH_3]_3$}. ^{31}P{^{1}H} NMR (−40 °C): 5.37 (s).

[Bis(triethylphosphine)nickelio]anthracene (1). A solution of $Cl_2Ni(PEt_3)_2$ (245.8 mg, 0.672 mmol) in THF (13 mL) was added to a stirred cold (−78 °C) suspension of magnesium–anthracene (409.8 mg, 0.956 mmol) in THF (7 mL). The stirred suspension was allowed to warm to −10 °C during 3 h, and the color changed from red to deep brown. The solvent was removed under vacuum (−10 to −20 °C), and cold hexane (50 mL) was added. The suspension was filtered (−40 °C), and the red-brown filtrate was kept at −80 °C for 4 days. The mother liquor was cannulated from the formed red crystals, which were washed with cold hexane (−78 °C, 2 × 10 mL) and dried on the vacuum line. The product is thermochromic and changes its color from bright red (−80 °C) to dark brown (room temperature), both as a solid and in solution. Yield: 41%. Additional product can be obtained from the mother liquor by concentrating to about half its volume and cooling it again. ^{1}H NMR (−30 °C): 7.58 (m, 2 H, H_5 and H_8), 7.36 (s, 2 H, H_9 and H_{10}), 7.11 (m, 2 H, H_6 and H_7), 5.39 (m, 2 H, H_1 and H_4), 5.30 (m, 2 H, H_2 and H_3), 1.56, 1.04, 0.80 [m, 30 H, P-(CH_2CH_3)]. ^{31}P{^{1}H} NMR (−30 °C): 20.4 (d) and 8.7 (d), J_{P-P} = 50.7. ^{13}C{^{1}H} NMR (−70 °C): 138.1, 132.4, 127.0, 123.7, 120.3 (C_5–C_{14}), 89.6 (d, J_{P-C} = 2), 85.8 (d, J_{P-C} = 9) (C_1–C_4), 21.5 (dd, J_{P-C} = 17, $J_{P'-C}$ = 2, P–CH_2CH_3), 18.1 (dd, $J_{P'-C'}$ = 18, $J_{P-C'}$ = 1, P′–$C'H_2C'H_3$), 12.1 (P–CH_2CH_3), 12.0 (P′–$C'_2C'H_3$). IR: 1930 (w), 1915 (w), 1895 (w), 1615 (w), 1258 (m), 1245 (m), 1092 (m), 1020 (s), 872 (m), 800 (s), 760 (s), 725 (m), 703 (m). Anal. Calcd: C, 65.99; H, 8.52; P, 13.09. Found: C, 66.32; H, 8.17; P, 13.29.

[Bis(tributylphosphine)nickelio]anthracene (2). The procedure is essentially the same as for the preparation of 1. However, concentration of the hexane solution to one-fourth its original volume was necessary in order to allow crystallization, and cooling to −105 °C was required in some runs. ^{1}H NMR (−30 °C): 7.55 (m, 2 H, H_5 and H_8), 7.42 (s, 2 H, H_9 and H_{10}), 7.15 (m, 2 H, H_6 and H_7), 5.34 (m, 2 H, H_1 and H_4), 5.27 (m, 2 H, H_2 and H_3), 1.43–1.54 [m, 18 H, P(CH_2)$_3$CH$_3$], 1.08–1.13 [m, 18 H, P-(CH_2)$_3$CH$_3$], 0.95 [ps t, 9 H, P(CH$_2$)$_3$$CH_3$], 0.82 [ps t, 9 H, P-(CH$_2$)$_3$$CH_3$]. ^{31}P{^{1}H} NMR (−30 °C): 11.1 (d) and 2.5 (d), J_{P-P} = 52.2. ^{13}C{^{1}H} NMR (−70 °C): 138.0, 132.5, 127.0, 123.7, 120.9 (C_5–C_{14}), 90.3, 75.8 (d, J_{P-C} = 8) (C_1–C_4), 28.1 27.8, 27.1, 26.9, 24.1, 23.9 [P–(CH_2)$_3$CH$_3$), 14.8 [P–(CH$_2$)$_3$$CH_3$]. IR: 1930 (w), 1917 (w), 1895 (w), 1875 (w), 1790 (w), 1617 (w), 1565 (w), 1290 (w), 1265 (m), 1240 (m), 1088 (w), 1042 (m), 1000 (w), 965 (w), 940 (w), 900 (s), 875 (s), 785 (s), 770 (s) 720 (s). Anal. Calcd: C, 71.14; H, 10.05; P, 9.66. Found: C, 71.01; H, 10.45; P, 9.50.

Typical NMR Experiment. An NMR tube (Wilmad 524 or 527) connected to a joint and fitted with a Schlenk adaptor was evacuated and filled with Ar. The studied material was transferred and weighted in the tube, the tube was evacuated, and THF-d_8 was vacuum-transferred into it, while being cooled with liquid N_2. After a sufficient amount of solvent was transferred, the tube was torch-sealed and kept at a temperature ≤−78 °C until studied. After the measurement the tube was allowed to reach room temperature, and the solution height in the NMR tube (H, cm) was measured. The solution volume (milliliters) was calculated according to the following formula:

$$V(527) = 0.1385H - 0.0152$$

$$V(524) = 0.06743H - 0.01027$$

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Registry No. 1, 135709-29-4; 2, 135709-32-9; $(Bu_3P)NiCl_2$, 15274-43-8; $(Et_3P)NiCl_2$, 17523-24-9; $NiCl_2$, 7718-54-9; Bu_3P, 998-40-3; magnesium–anthracene–$(THF)_3$, 86901-19-1; anthracene, 120-12-7.