Synthesis and Single-Crystal X-ray Study of the Mononuclear η^2-Benzyne (Dehydrobenzene) Nickel(0) Complex $Ni(\eta^2\text{-}C_6H_4)((C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2)$. Insertion Reactions with Simple Molecules and X-ray Crystal Structure of the Nickelaindan Complex $\overline{Ni(CH_2CH_2C}_6H_4\text{-}o)((C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2)$

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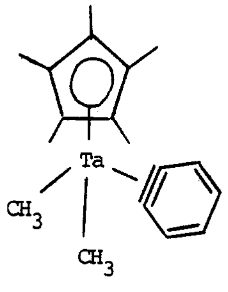
Received February 20, 1985

Sodium amalgam reduction of $NiCl(C_6H_4Br\text{-}2)(Cy_2PCH_2CH_2PCy_2)\cdot 0.5THF$ (**6**) (Cy = cyclohexyl, C_6H_{11}) gives a mononuclear nickel(0) complex, $Ni(\eta^2\text{-}C_6H_4)(Cy_2PCH_2CH_2PCy_2)$ (**3**), which has been characterized by microanalysis, by mass, infrared, and NMR (^1H, ^{13}C, ^{31}P) spectroscopy, and by single-crystal X-ray structural analysis. Crystals of **3** are orthorhombic, space group *Pbca*, with $a = 16.068$ (1) Å, $b = 17.189$ (1) Å, $c = 22.358$ (1) Å, and $Z = 8$. The structure was solved by heavy-atom methods and refined by least-squares methods to $R = 0.035$ and $R_w = 0.055$ for 4203 independent reflections. The molecule consists of a central nickel atom coordinated by a symmetric η^2-benzyne ligand [Ni–C(1) = 1.870 (4) Å, Ni–C(2) = 1.868 (4) Å], the coordination geometry being close to trigonal planar. The coordinated C–C bond length of 1.332 (6) Å is significantly larger than those observed in alkyne complexes of zerovalent nickel and platinum. The remaining C–C bonds of the six-membered ring are almost equal in length (average 1.385 Å), consistent with a delocalized aromatic structure for the benzyne ligand. Complex **3** reacts with iodine and methyl iodide at room temperature to give, respectively, the 2-iodophenyl and *o*-tolyl complexes $NiI(C_6H_4Y\text{-}2)(Cy_2PCH_2CH_2PCy_2)$ (Y = I (**7**), Me (**8**)). Carbon dioxide, ethylene, and dimethyl acetylenedicarboxylate insert into the nickel–benzyne bond of **3** to give the nickelacycles $\overline{Ni(C_6H_4COO)}(Cy_2PCH_2CH_2PCy_2)$ (**10**), $\overline{Ni(CH_2CH_2C}_6H_4\text{-}o)(Cy_2PCH_2CH_2PCy_2)$ (**11**), and $\overline{Ni(C(CO_2Me){=}C(CO_2Me)C}_6H_4\text{-}o)(Cy_2PCH_2CH_2PCy_2)$ (**12**), respectively, whereas diphenylacetylene displaces benzyne to give $Ni(PhC{\equiv}CPh)(Cy_2PCH_2CH_2PCy_2)$ (**13**). Crystals of **11** are monoclinic, space group $P2_1/n$, with $a = 15.792$ (6) Å, $b = 17.471$ (6) Å, $c = 12.104$ (4) Å, $\beta = 104.09$ (2)°, and $Z = 4$. The structure was solved and refined as for **3** to $R = 0.070$ and $R_w = 0.071$ for 2379 independent reflections. The nickel atom is coordinated in an approximately planar arrangement by the bidentate di(tertiary phosphine) and by two carbon atoms of a five-membered, half-chair-shaped chelate ring, the Ni–C(aryl) and Ni–C(alkyl) bond lengths being 1.951 (12) and 1.988 (12) Å, respectively.

Introduction

Although several *o*-phenylene complexes containing the C_6H_4 unit bound to two[1] or three[2] transition-metal atoms are known, there is only one structurally characterized mononuclear complex of benzyne (dehydrobenzene), viz., $Ta(\eta\text{-}C_5Me_5)Me_2(\eta^2\text{-}C_6H_4)$ (**1**), which is formed by thermal



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elimination of methane from $Ta(\eta\text{-}C_5Me_5)(C_6H_5)Me_3$;[3,4] the corresponding niobium compound is probably isostructural. A series of bis(benzyne) complexes of niobium, tantalum, molybdenum, and tungsten has been isolated from the reaction of the hexaarylmetalate anions with an excess of aryllithium.[5,6] The tantalum compound $[Li(OEt_2)]_3[Ta(C_6H_5)_4(C_6H_4)_2]$ has been assigned either a square-antiprismatic or dodecahedral structure, with facial η^2-C_6H_4 ligands, on the basis of variable-temperature ^1H and ^7Li NMR spectroscopy.[6] Benzyne complexes that are generally assumed to be mononuclear are likely intermediates in the thermal decomposition of $M(\eta\text{-}C_5H_5)_2(aryl)_2$ (M = Ti,[7] Zr[8]) and of other polyaryls of the early transition elements.[9] The evidence for their existence in these cases is based largely on the results of labeling experiments and on the isolation of the expected insertion products when the decompositions are carried out in the presence of

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[1] (a) $[Pt_4(\mu\text{-}C_6H_4)_2Cl_{14}]^{2-}$: Cook, P. M.; Dahl, L. F.; Dickerhoof, D. N. *J. Am. Chem. Soc.* **1972**, *94*, 5511. (b) $Ir_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C_6H_4)(CO)_2$: Rausch, M. D.; Gastinger, R. G.; Gardner, S. A.; Brown, R. K.; Wood, J. S. *Ibid.* **1977**, *99*, 7870.

[2] (a) $Os_3(CO)_7(\mu\text{-}PPh_2)_2(\mu_3\text{-}C_6H_4)$: Bradford, C. W.; Nyholm, R. S.; Gainsford, G. J.; Guss, J. M.; Ireland, P. R.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1972**, 87. (b) $HOs_3(CO)_7(\mu\text{-}PPh_2)(PPh_3)(\mu_3\text{-}C_6H_4)$: Gainsford, G. J.; Guss, J. M.; Ireland, P. R.; Mason, R.; Bradford, C. W.; Nyholm, R. S. *J. Organomet. Chem.* **1972**, *40*, C70. (c) $H_2Os_3(CO)_9(\mu_3\text{-}C_6H_4)$: Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415. (d) $Ru_3(CO)_7(\mu\text{-}PPh_2)_2(\mu_3\text{-}C_6H_4)$: Bruce, M. I.; Shaw, G.; Stone, F. G. A. *Ibid.* **1972**, 2094.

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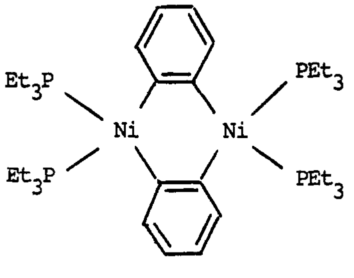
0276-7333/85/2304-1992$01.50/0

trapping agents, such as olefins,[10] acetylenes,[11] carbon dioxide,[12] and dinitrogen.[13]

In view of the high affinity of d^{10} zerovalent metal complexes for alkynes, including strained cyclic alkynes,[14] it is surprising that all attempts to form benzyne complexes of nickel(0) or platinum(0) have been unsuccessful,[15] despite an early claim[16] that subsequently proved to be incorrect.[17] A promising approach to the problem was made by Miller et al.[18] who showed that the (2-bromophenyl)nickel(II) complex *trans*-NiCl(C_6H_4Br-2)(PEt_3)$_2$ is reduced by lithium in ether to give a thermally unstable material of empirical formula Ni(C_6H_4)(PEt_3)$_2$, for which the dimeric μ-*o*-phenylene structure **2** was suggested on the basis of ^{1}H NMR and molecular weight data. This result suggested that use of a bulky bidentate di(tertiary phosphine) in place of triethylphosphine in this system might favor an η^2-benzyne over a μ-*o*-phenylene structure and would eliminate problems arising from ligand dissociation in **2**.[18] In this paper we report on the preparation, structural characterization, and chemistry of the monomeric, η^2-benzyne nickel(0) complex Ni(η^2-C_6H_4)($Cy_2PCH_2CH_2PCy_2$).[19]



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Experimental Section

General Procedures. All reactions were performed in a nitrogen atmosphere with use of standard Schlenk techniques and freshly distilled, dry solvents.

The following instruments were used for NMR measurements with an internal deuterium lock: JEOL FX200 (^{1}H; ^{13}C at 50.10 MHz), JEOL FX60 (^{31}P at 24.3 MHz), and Bruker CXP200 (^{13}C at 50.29 MHz, ^{31}P at 80.98 MHz). The ^{13}C{^{1}H} spectrum of the benzyne complex **3** was recorded on a Bruker HFX 270 instrument. Some ^{31}P spectra were obtained for solutions in nondeuterated solvents by use of an external D_2O lock. Chemical shifts (δ) are reported in parts per million downfield (to high frequency, taken as positive) of internal $(CH_3)_4Si$ (^{1}H, ^{13}C) or of external 85% H_3PO_4 (^{31}P). Infrared spectra were measured on a Perkin Elmer 683 instrument.

Analyses were carried out in the microanalytical laboratories of this School (Miss Brenda Stevenson and associates).

Starting Materials. 1,2-Bis(dichlorophosphino)ethane was bought from Strem Chemicals Inc. and converted into 1,2-bis(dicyclohexylphosphino)ethane, $Cy_2PCH_2CH_2PCy_2$, by the action of cyclohexylmagnesium chloride.[20] The orange-red nickel(II) complex $NiCl_2(Cy_2PCH_2CH_2PCy_2)$ was prepared by addition of the di(tertiary phosphine), dissolved in the minimum volume of dichloromethane, to ethanolic $NiCl_2{\cdot}6H_2O$.[21] Often the nickel complex was made directly, without isolating the pure ligand, by siphoning the ether layer obtained from the preparation[20] into ethanolic $NiCl_2{\cdot}6H_2O$; the yield was ca. 60%.

The nickel(0)-ethylene complex $Ni(C_2H_4)(Cy_2PCH_2CH_2PCy_2)$ (**4**) has been made previously by addition of the di(tertiary phosphine) to Ni(*t*,*t*,*t*-1,5,9-cyclododecatriene) in an atmosphere of ethylene.[22] We made it more simply as follows.

A quantity of $NiCl_2(Cy_2PCH_2CH_2PCy_2)$ (8.3 g, 15.0 mmol), lithium dispersion (0.71 g of 36% w/w dispersion, 36 mmol), and THF (50 mL) were placed in a Schlenk tube together with a stirring bar and some rough glass beads of 6 mm diameter occupying ca. 10 mL. The mixture was stirred vigorously, and ethylene was bubbled through it until no more was absorbed (2–3 h) and a yellowish solution containing some crystals had been formed. The mixture was evaporated to dryness, and the residue was washed with ether (2 × 20 mL). It was extracted with hot toluene (80 mL), and the solution was filtered and evaporated to a volume of ca. 40 mL. Addition of deoxygenated ethanol (60 mL) gave a crystalline slurry. This was set aside at 0 °C and filtered, and the bright yellow crystalline solid was washed with ethanol (2 × 20 mL). After drying in vacuo, there was obtained 6.7 g (88%) of **4**.

Reactions of 4. (a) With Trifluoroacetic Acid. A stirred suspension of **4** (0.15 g, 0.30 mmol) in cyclohexane (4 mL) was treated with CF_3CO_2H (45 μL, 0.60 mmol). After 2 h the yellow solid was filtered off, washed with hexane (3 × 2 mL), and recrystallized from dichloromethane (0.3 mL) by addition of hexane (3 mL). The yellow, crystalline solid was dried at 80 °C in vacuo to give $Ni(O_2CCF_3)_2(Cy_2PCH_2CH_2PCy_2)$ (0.18 g, 0.25 mmol. 86%): ^{1}H NMR ($CDCl_3$) δ 1.0–2.84 (m, CH_2 and C_6H_{11}); ^{31}P{^{1}H} NMR (CH_2Cl_2) δ 79.0 (s). Calcd for $C_{30}H_{48}F_6NiO_4P_2$: C, 50.9; H, 6.8; F, 16.1; P, 8.8. Found: C, 50.6; H, 6.9; F, 15.7; P, 8.9.

(b) With Iodobenzene. A mixture of **4** (1.54 g, 3.0 mmol) and iodobenzene (0.38 mL, 3.4 mmol) in benzene (4 mL) was stirred and heated at 50 °C for 0.5 h. Gas was given off and a yellow precipitate formed. Hexane (20 mL) was added, and the yellow solid was filtered off, washed with hexane, and dried. It was dissolved in dichloromethane (50 mL), and the resulting orange solution was filtered, treated with methanol (140 mL), and allowed to stand overnight at room temperature. The orange-red crystals of $NiI(C_6H_5)(Cy_2PCH_2CH_2PCy_2)$ (**9**) were filtered off and dried in vacuo: yield 1.74 g (84%); mp 185 °C; ^{1}H NMR (CD_2Cl_2) δ 0.68–2.53 (m, 48, CH_2 and C_6H_{11}), 6.70 (t, 1), 6.93 (t, 2), 7.45 (t, 2) (C_6H_5); ^{31}P{^{1}H} NMR (CH_2Cl_2) δ 64.7, 69.2 (ABq, J = 19.5 Hz). Anal. Calcd for $C_{32}H_{53}INiP_2$: C, 56.1; H, 7.8; I, 18.5; Ni, 8.6. Found: C, 56.1; H, 8.0; I, 18.5; Ni, 8.3.

(c) With *o*-Bromotoluene. A mixture of *o*-bromotoluene (2 mL, 16.6 mmol) and **4** (1.84 g, 3.6 mmol) was heated at 90 °C for 15 min. Gas was evolved, and orange-brown crystals were formed. After it had cooled to room temperature, the mixture was diluted with methanol (30 mL) and filtered. The orange solid was dissolved in dichloromethane (10 mL), and the resulting solution was chromatographed on a 10 in. × 1$^1/_2$ in. column of acidic alumina (activity 1). The leading yellow band that eluted with 4:1 dichloromethane/ether was collected and evaporated to dryness. The resulting gum was taken up in hot THF (20 mL), and the filtered solution was treated with a hot solution of LiBr (0.5 g) in methanol (10 mL). Water was added until the solution just turned cloudy. The orange, crystalline solid that deposited on cooling was the bromo complex NiBr(C_6H_4Me-2)-

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[19] Abbreviation: Cy = cyclohexyl, C_6H_{11}.

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($Cy_2PCH_2CH_2PCy_2$), mp 203–230 °C dec (1.6 g, 2.5 mmol, 68%).

A sample of $NiBr(C_6H_4Me\text{-}2)(Cy_2PCH_2CH_2PCy_2)$ (0.20 g, 0.31 mmol) was dissolved in hot THF (10 mL) and treated with a solution of NaI (0.5 g, 3.3 mmol) in methanol (3 mL). The mixture was diluted with water until it just turned cloudy. The orange-brown crystals that deposited were filtered off, washed with water and methanol, and dried at 100 °C (0.1 mm) for 3 h to give $NiI(C_6H_4Me\text{-}2)(Cy_2PCH_2CH_2PCy_2)$ (**8**): mp 200 °C dec (0.20 g, 0.29 mmol, 93%); ^1H NMR (CD_2Cl_2) δ 0.87–2.56 (m, 48, CH_2 and C_6H_{11}), 2.75 (s, 3, Me), 6.54–7.27 (m, 4, C_6H_4); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 19.5–36.9 (m, CH_2 and C_6H_{11}), 28.5 (s, Me), 122.1, 137.4 (each s, aromatic CH), 123.8, 127.9 (each d, aromatic CH), 145.4 (s, *C*Me), 154.4 (4-line m, separations = 80.5, 32.2 Hz, CNi); $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 61.3, 65.4 (ABq, J = 17.1 Hz). Anal. Calcd for $C_{33}H_{55}IP_2Ni$: C, 56.7; H, 7.9; I, 18.2; P, 8.9. Found: C, 56.7; H, 7.8; I, 18.0; P, 9.2.

(d) With *o*-Diiodobenzene. *o*-Diiodobenzene (1.0 mL, 7.7 mmol) and toluene (0.5 mL) were added to **4** (0.53 g, 1.05 mmol), and the mixture was stirred for 1 h at room temperature. Addition of hexane (20 mL) gave an orange-brown solid that was filtered off and washed with hexane (2 × 10 mL). This was dissolved in dichloromethane and rapidly chromatographed on a 5 in. × 1 in. column of acidic alumina. The amber forerun was collected and evaporated to an orange oil which crystallized on addition of hexane (10 mL). The solid was recrystallized from dichloromethane (6 mL) by addition of hexane (15 mL) to give orange-brown crystals of $NiI(C_6H_4I\text{-}2)(Cy_2PCH_2CH_2PCy_2)$ (**7**): mp 180–200 °C dec (0.65 g, 0.80 mmol, 76%); ^1H NMR (CD_2Cl_2) δ 0.73–3.3 (m, 48, CH_2 and C_6H_{11}), 6.27–7.50 (m, 4, C_6H_4); $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 61.6, 64.2 (ABq, J = 24.1 Hz). Anal. Calcd for $C_{32}H_{52}I_2NiP_2$: C, 47.4; H, 6.5; Ni, 7.2. Found: C, 47.4; H, 6.5; Ni, 6.9.

(e) With *o*-Dibromobenzene. A mixture of *o*-dibromobenzene (15 g, 64 mmol) and cyclohexane (5 mL) was added to **4** (9.4 g, 18.5 mmol), and the mixture was stirred under nitrogen. At periodic intervals the IR spectrum of a portion of the mixture was measured as a smear between KBr plates. After 26 h the peaks at 3015 and 1165 cm^{-1} due to **4** had disappeared. The thick brown slurry was then diluted with hexane (100 mL), stirred thoroughly, and filtered. The resulting orange solid was washed with hexane (3 × 50 mL) and dried. It was dissolved in dichloromethane (100 mL), and the solution was filtered through Celite and then chromatographed through a 16 in. × $1^3/_4$ in. column of acidic alumina (activity 1) made up with dichloromethane. Most of the leading yellow band was eluted with this solvent, and the rest was eluted with ether/dichloromethane (1:30). The combined yellow eluates were evaporated to dryness, and the residual gum was dissolved in hot THF (150 mL) and treated with a solution of LiCl (3 g) in methanol (50 mL). The solution was diluted with water (ca. 70 mL) until just cloudy and set aside overnight. The resulting golden flakes were filtered off, washed successively with methanol, water, and methanol again, and dried in vacuo to give $NiCl(C_6H_4Br\text{-}2)(Cy_2PCH_2CH_2PCy_2)\cdot 0.5$ THF (**6**): mp 205 °C dec (6.9 g, 9.7 mmol, 52%); ^1H NMR ($CDCl_3$) δ 0.90–3.33 (m, 50, CH_2, C_6H_{11} and THF), 3.70 (m, 2, CH_2 of THF), 6.53–7.27 (m, 4, C_6H_4); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 18.0–37.0 (m, CH_2, C_6H_{11} and THF), 68.2 (s, CH_2 of THF), 124.4 (s), 125.1 (d), 130.9 (s), 138.9 (d) (aromatic CH), 134.9 (s, CBr), 161.2 (4-line m, CNi); $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 64.6 (s). Anal. Calcd for $C_{34}H_{56}BrClNiO_{0.5}P_2$: C, 57.6; H, 8.0; Br, 11.3; Cl, 5.0; P, 8.7. Found: C, 57.2; H, 8.1; Br, 11.2; Cl, 5.0; P, 8.8.

(f) With Diphenylacetylene. Benzene (7 mL) was added to a mixture of **4** (0.86 g, 1.70 mmol) and diphenylacetylene (0.33 g, 1.86 mmol). The effervescing mixture was stirred for 5 min, and the yellow solution was then evaporated to ca. 3-mL volume. Dilution with pentane (5 mL) gave rosettes of orange-yellow prisms. These were recrystallized from hot toluene (3 mL) by addition of hexane (9 mL) and dried in vacuo at 80 °C for 3 h to give $Ni(PhC{\equiv}CPh)(Cy_2PCH_2CH_2PCy_2)$ (**13**): mp 180–182 °C (0.92 g, 1.31 mmol, 77%); ^1H NMR (C_6D_6) δ 0.65–1.90 (m, 48, CH_2 and C_6H_{11}), 6.55–7.05 (m, 10, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 22.6 (t, P*C*H_2), 26.6–30.2 (m, cyclohexyl CH_2), 36.0 (t, PCH), 124.7 (s), 127.5 (s), 128.2 (s) (aromatic CH), 139.2 (t, separation between outer lines = 41 Hz), 140.9 (t, separation between outer lines = 16.2 Hz) (*C*C≡C and *C*≡C); $^{31}P\{^1H\}$ NMR (C_6H_6) δ 69.7 (s); IR (Nujol) 1771 s (C≡C) cm^{-1}. Anal. Calcd for $C_{40}H_{58}NiP_2$: C, 72.8; H, 8.9; Ni, 8.9. Found: C, 73.2; H, 9.2; Ni, 8.5.

Preparation of (Benzyne)(1,2-bis(dicyclohexylphosphino)ethane)nickel(0), $Ni(\eta^2\text{-}C_6H_4)(Cy_2PCH_2CH_2PCy_2)$ (3). A mixture of **6** (3.0 g, 4.23 mmol) and sodium amalgam (78 g, 0.5% w/w, 16 mmol) in THF (30 mL) was stirred for 3.5 h. The amber solution was evaporated to dryness, and the residue was extracted with hot cyclohexane (15 mL). The solution was filtered and evaporated to dryness to give an orange oil that crystallized when it was triturated with hexane (15 mL). The solid was redissolved in hot cyclohexane (17 mL), and the solution was filtered and evaporated to small volume. Addition of hexane (10 mL) gave a yellow crystalline solid. This was filtered off and washed with hexane (3 × 3 mL) to give **3**: mp 140 °C dec (1.68 g, 3.03 mmol, 72%); ^1H NMR (C_6D_6) δ 0.87–2.16 (m, 48, CH_2 and C_6H_{11}), 7.42, 8.08 (m, 4, C_6H_4) (collapses to AA′BB′ pattern on ^{31}P decoupling); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 22.2 (t, CH_2P, separation between outer lines = 4 Hz), 26.6, 27.6, 29.6, 29.9 (each s, CH_2 of C_6H_{11}), 35.2 (t, CHP, separation between outer lines = 2.3 Hz), 125.7 (t, aromatic CH), 127.5 (s, aromatic CH), 145.4 (5-line m, aromatic C); $^{31}P\{^1H\}$ NMR (THF) δ 77.6 (s); IR (KBr) 1583 s (coordinated $C\overset{\dots}{=}C$) cm^{-1}. Anal. Calcd for $C_{32}H_{52}NiP_2$: C, 69.0; H, 9.4; P, 11.1; mol wt, 557. Found: C, 68.6; H, 9.4; P, 11.1; mol wt, 531 ± 50 (cryoscopy in benzene, mean of three determinations).

Reactions of 3. (a) With Trifluoroacetic Acid. Trifluoroacetic acid (14 μL, 0.19 mmol) was injected into a solution of **3** (51.7 mg, 0.093 mmol) in THF (0.33 mL) in an NMR tube. The initial yellow color deepened. After 15 min the only signal in the aromatic region of the ^1H NMR spectrum was a sharp singlet at δ 7.28 assigned to benzene. The solution was evaporated, and the vapors were collected in a trap cooled to 78 K. The colorless condensate showed only peaks due to C_6H_6 at δ 7.28 and to THF in its ^1H NMR spectrum and its GC/MS confirmed the presence of benzene. The yellow crystalline residue from evaporation of the reaction mixture was identified as $Ni(O_2CCF_3)_2(Cy_2PCH_2CH_2PCy_2)$ by comparison of its ^1H and $^{31}P\{^1H\}$ NMR spectra with those of authentic material (see above).

(b) With Iodine. A solution of iodine (0.052 g, 0.205 mmol) in THF (0.5 mL) was added dropwise to a stirred solution of **3** (0.114 g, 0.205 mmol) in THF (1 mL) at −20 °C to give a red-brown solution. When the solution was allowed to warm to room temperature, orange crystals precipitated. The mixture was diluted with hexane (5 mL) and filtered to give $NiI(C_6H_4I\text{-}2)(Cy_2PCH_2CH_2PCy_2)$ (**7**) as an orange crystalline solid (0.15 g, 91%). The $^{31}P\{^1H\}$ NMR spectrum of the compound showed an AB quartet at δ 61.6 and 64.3 (J = 24.4 Hz), identical within experimental error with that of the authentic material (see above).

(c) With Methyl Iodide. The benzyne complex **3** (0.05 g, 0.09 mmol) was dissolved in an excess of pure, dry methyl iodide (0.33 mL) in an NMR tube. Monitoring of the aromatic region of the ^1H NMR spectrum showed that the reaction was over after ca. 30 min at room temperature. The deep red solution was evaporated to dryness, and the crystalline residue was dissolved in $CDCl_3$. The $^{31}P\{^1H\}$ NMR spectrum showed the presence of $NiI(C_6H_4Me\text{-}2)(Cy_2PCH_2CH_2PCy_2)$ (**8**) [δ 61.4, 65.5 (J_{AB} = 17.1 Hz)] (ca. 95%), together with ca. 5% of $NiI(C_6H_5)(Cy_2PCH_2CH_2PCy_2)$ (**9**) [δ 64.6, 69.2 (J_{AB} = 19.5 Hz)] and a trace of $NiI_2(Cy_2PCH_2CH_2PCy_2)$ [δ 97.1 (s)]. The ^1H NMR spectrum showed a singlet at δ 2.77 due to the tolyl methyl group of **8**. Its intensity relative to the four proton aromatic multiplet at δ 6.5–7.5 was ca. 2.8.

(d) With Carbon Dioxide. A sample of **3** (0.30 g, 0.54 mmol) was put under an atmosphere of CO_2 in a Schlenk tube attached to a gas buret and manometer. Carbon dioxide saturated THF (3 mL) was injected into the Schlenk tube, the manometer was leveled quickly to allow for solvent vapor pressure, and the mixture was stirred with a magnetic stirring bar. The complex dissolved and gas was absorbed rapidly. After 2 min, when absorption had ceased, the manometer was again leveled and the volume of CO_2 was measured again. The volume of CO_2 absorbed was 13.4 mL at 301 K (0.953 atm), corresponding to ca. 0.57 mmol, i.e., 1 mol/mol of **3**. The yellow solution was diluted gradually with hexane (6 mL) to give lemon yellow crystals of $\overline{Ni(C_6H_4COO)}(Cy_2PCH_2CH_2PCy_2)$ (**10**): mp 235 °C dec (0.28 g, 87%). ^1H NMR (CD_2Cl_2) δ 1.33–2.58 (m, 48, CH_2 and C_6H_{11}), 6.92–7.41 (m, 4, C_6H_4); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 16.6–36.7 (m, CH_2 and C_6H_{11}), 124.4 (s), 127.7 (s), 130.0 (d), 136.6 (m) (aromatic CH), 144.3 (s, CCO_2), 154.4 (dd, separations = 79.7, 28.0 Hz, CNi), 182.5 (d, CO_2, J = 13.6 Hz); $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 68.0, 75.7 (ABq, J = 26.9 Hz). Anal. Calcd for $C_{33}H_{52}NiO_2P_2$: C, 65.9; H, 8.7; P, 10.3. Found: C, 66.0; H, 8.8; P, 10.4.

A stirred solution of **10** (0.24 g, 0.40 mmol) in dry dichloromethane (3 mL) was treated dropwise with CF_3CO_2H (67 μL, 0.87 mmol). Evaporation of the orange solution gave a yellow crystalline residue which was washed with dry ether (10 mL). The residual solid was recrystallized from dichloromethane/hexane to give yellow crystals of $Ni(O_2CCF_3)_2(Cy_2PCH_2CH_2PCy_2)$ (0.27 g, 0.38 mmol, 95%), identified by its $^{31}P\{^1H\}$ NMR spectrum. The ether extract, on evaporation to dryness, gave a pale yellow solid which gave a white, crystalline sublimate at 65 °C (0.01 mm). This was identified as benzoic acid (0.032 g, 0.26 mmol, 65%) by melting point and mixed melting point.

(e) With Ethylene. A solution of **3** (0.32 g, 0.58 mmol) in cyclohexane (8 mL) was stirred at 80 °C for 4 h under ethylene (3 torr) in a Fisher-Porter vessel. The orange-brown solution was evaporated to dryness. The residue was taken up in benzene (1 mL), and the solution was stirred until crystals formed. The mixture was diluted with pentane (10 mL), cooled to −10 °C, and filtered. The yellow-brown solid was dissolved in benzene (5 mL), and the solution was diluted rapidly with pentane (10 mL). A brown flocculent precipitate was removed by filtration. The yellow filtrate was evaporated to ca. 2 mL, diluted with pentane (8 mL), and stirred until crystals formed. The mixture was cooled to 0 °C and filtered to give orange-yellow crystals of $\overline{Ni(CH_2CH_2C_6H_4}\text{-}o)(Cy_2PCH_2CH_2PCy_2)$ (**11**): mp 180–210 °C dec (0.17 g, 0.29 mmol, 50%). ^1H NMR (C_6D_6) δ 0.87–2.42 (m, 50, CH_2 and C_6H_{11}), 3.60 (m, 2, CH_2), 7.1–8.0 (m, 4, C_6H_4). $^{13}C\{^1H\}$ NMR (C_6D_6) δ 20.9–36.2 (m, CH_2 and C_6H_{11}), 45.25 (4-line m, CH_2Ni) (assignment as a CH_2 group confirmed by INEPT experiment), 121.9 (s), 122.5 (d), 123.6 (s), 141.0 (m) (aromatic CH), 163.7 (d, CCH_2, J = 5.8 Hz), 169.4 (dd, separations = 81.0, 15.0 Hz, CNi); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 63.6 (s), 65.5 (s); mass spectrum, m/z 584 (parent ion). Anal. Calcd for $C_{34}H_{56}NiP_2$: C, 69.8; H, 9.6; P, 10.6. Found: C, 69.8; H, 9.5; P, 10.6.

(f) With Dimethyl Acetylenedicarboxylate. A stirred solution of **3** (0.34 g, 0.61 mmol) in THF (4.5 mL) was cooled to −10 °C and treated slowly with a solution of dimethyl acetylenedicarboxylate (75 μL, 0.61 mmol) in THF (1.5 mL). The yellow solution turned orange and an orange solid precipitated. The mixture was stirred for 30 min, diluted gradually with hexane (5 mL), and filtered. The solid was washed with hexane (3 × 2 mL) and dried in vacuo to give $\overline{Ni(C(CO_2Me){=}C(CO_2Me)\text{-}}$ $C_6H_4\text{-}o)(Cy_2PCH_2CH_2PCy_2)$ (**12**) as a microcrystalline orange powder (0.36 g, 0.51 mmol, 85%). The analytical sample was recrystallized from hot THF (ca. 2.5 mL) by addition of hexane (12 mL) and was dried at 80 °C (0.01 mm) for 5 h. The orange crystals of **12** melted at 186 °C: ^1H NMR (CD_2Cl_2) δ 1.0–2.6 (m, 48, CH_2 and C_6H_{11}), 3.67 (s, 3, Me), 3.70 (s, 3, Me), 6.65–7.15 (m, 4, C_6H_4); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 17.5–38.0 (m, CH_2 and C_6H_{11}), 51.2 (s, Me), 51.4 (s, Me), 122.1 (s), 124.2 (s), 125.1 (d), 138.6 (q) (aromatic CH), 148.8 (d, J =11 Hz), 158.5 (d, J = 5.9 Hz), 162.4 (dd, separations = 50.0, 25.0 Hz), 166.5 (d, J = 2 Hz), 169.6 (dd, separations = 65.0, 18.0 Hz) (aromatic CNi, aromatic $CC{=}C$, $C{=}CNi$, $C{=}CNi$, CO_2Me), 179.8 (approx t, separation between outer lines = 8 Hz, CO_2Me); $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 61.7, 68.1 (ABq, J = 19.5 Hz); IR (KBr) 1710 s (ester), 1533 s (C=C) cm^{-1}. Anal. Calcd for $C_{38}H_{58}NiO_4P_2$: C, 65.3; H, 8.4; Ni, 8.4. Found: C, 65.3; H, 8.6; Ni, 8.2.

(g) With Diphenylacetylene. A solution containing **3** (49 mg) and diphenylacetylene (15.7 mg) (1:1 mole ratio) in benzene-d_6 was sealed in an NMR tube, and the $^{31}P\{^1H\}$ NMR spectrum was recorded periodically. After 1 week at 20 °C little reaction had taken place, although there was a small singlet at δ 69.9 due to $Ni(PhC{\equiv}CPh)(Cy_2PCH_2CH_2PCy_2)$ (**13**). After heating at 80 °C for 7.5 h, there were singlets due to **3** and **13** at δ 77.4 and 69.8 in a 1:3 ratio and singlets at δ 61.2 and 48.7 due to traces of unknown byproducts.

The reaction was carried out on a preparative scale as follows. A solution containing **3** (0.33 g, 0.59 mmol) and diphenylacetylene (0.11 g, 0.62 mmol) in benzene (2.5 mL) was heated at 80 °C for 7.5 h. The amber solution was evaporated to ca. 2 mL, diluted with pentane (3 mL), and alternately cooled in liquid nitrogen and allowed to warm until yellow crystals formed. Addition of more pentane (9 mL) gave a yellow-orange solid. This was dissolved in benzene (1 mL), and the solution was diluted with pentane (2 mL). A small amount of dark solid was removed by filtration. Addition of pentane (8 mL) to the filtrate gave **13** as yellow fronds (0.23 g, 0.35 mmol, 60%). It was identical (IR and NMR spectroscopy) with the complex prepared from **4** (see above).

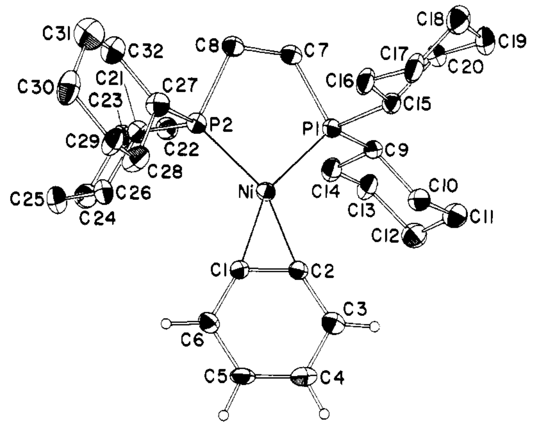

Figure 1. Molecular structure of $Ni(\eta^2\text{-}C_6H_4)(Cy_2PCH_2CH_2PCy_2)$. Thermal ellipsoids depict 30% probability surfaces. Methylene and methine hydrogen atoms of the phosphine ligand have been omitted for clarity.

Single crystals of $Ni(\eta^2\text{-}C_6H_4)(Cy_2PCH_2CH_2PCy_2)$ (**3**) and of $\overline{Ni(CH_2CH_2C_6H_4}\text{-}o)(Cy_2PCH_2CH_2PCy_2)$ (**11**) were grown from dioxane and from benzene/hexane, respectively.

Crystal Data. **3**: $C_{32}H_{52}NiP_2$, formula wt 557.43, orthorhombic, space group $Pbca$, a = 16.068 (1) Å, b = 17.189 (1) Å, c = 22.358 (1) Å, D_{measd} = 1.20 (1) g cm^{-3}, D_{calcd} = 1.199 g cm^{-3}, Z = 8, μ(Cu K$\bar{\alpha}$) = 19.15 cm^{-1}.

11: $C_{34}H_{56}NiP_2$, formula wt 585.48, monoclinic, space group $P2_1/n$, a = 15.792 (6) Å, b = 17.471 (6) Å, c = 12.104 (4) Å, β = 104.09 (2)°, D_{measd} = 1.20 (1), D_{calcd} = 1.201 g cm^{-3}, Z = 4, μ(Cu K$\bar{\alpha}$) = 19.00 cm^{-1}.

Reflection intensities for both complexes were recorded at ambient temperature using crystal monochromated Cu K$\bar{\alpha}$ radiation. The structures were solved by conventional Patterson and Fourier synthesis techniques and were refined by full-matrix least-squares analysis. Benzyne hydrogen atom coordinates were refined. Methylene and methine hydrogen atoms were included in the scattering model with coordinates located by calculation (C–H = 0.97 Å) and not subsequently refined. Calculations were performed with SHELX-76[23] and ANUCRYS[24] programs. At convergence R = 0.035 and R_w = 0.055 for **3** [4203 reflections, $I \geq 2.5\sigma(I)$] and R = 0.070 and R_w = 0.071 for **11** [2397 reflections, $I \geq 2.5\sigma(I)$]. Experimental details are summarized in Table I, and refinement details are summarized in Table II. Selected bond lengths and interbond angles for **3** and for **11**, respectively, are listed in Tables III and IV. Tables V (**3**) and V (**11**), atomic coordinates and thermal parameters, and Tables VI (**3**) and VI (**11**), observed and calculated structure factors, have been deposited. The atomic nomenclature is defined in Figures 1 and 2 (methylene and methine hydrogen atoms, omitted for clarity, are named as for attached carbon atoms). The figures were drawn with ORTEP.[25]

Results and Discussion

Oxidative addition of o-dibromobenzene to the (ethylene)nickel(0) complex $Ni(\eta^2\text{-}C_2H_4)(Cy_2PCH_2CH_2PCy_2)$ (**4**)

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Table I. Data Collection Details

	$\mathrm{Ni(\eta^2\text{-}C_6H_4)(Cy_2PCH_2CH_2PCy_2)}$	$\mathrm{\overline{Ni(CH_2CH_2C}_6H_4\text{-}\mathit{o})(Cy_2PCH_2CH_2PCy_2)}$
diffractometer	Picker FACS-1	Philips PW1100
radiation	Cu K$\bar{\alpha}$ (1.5418 Å)	
monochromator	graphite crystal	
scan type	θ-2θ	
scan speed, deg min^{-1}	2 (2θ)	
background	2 × 10 s	
2θ scan limit, deg	128	120
"standard" reflctns	3 every 97 reflections	3 every 60 min
indices	(14, 0, 0), (0, 10, 0), (0, 0, 12)	(90$\bar{1}$), ($\bar{2}$83), (006)
cryst stability	8.6-11.7% anisotropic decay during data collectn	30.2-33.9% anisotropic decay during data collectn
total reflctns scanned	5857	5520
unique reflctns with $I \geq 2.5\sigma(I)$	4203	2379
R_s[a]	0.015	0.045
R_{int}[b]	N/A	0.029 (700 pairs)
cryst dimens, mm	0.25 × 0.27 × 0.30	0.20 × 0.05 × 0.15
cell dimens determinatn	12 reflectns, FACS-1 diffractometer, λ = 1.540 51 Å, 80 < 2θ < 112°, t = 20 ± 2 °C	12 reflectns, FACS-1 diffractometer, λ = 0.709 26 Å, 26 < 2θ < 38°, t = 20 ± 2 °C

[a] $R_s = \Sigma\sigma(F_o)/\Sigma|F_o|$. [b] $R_{int} = \Sigma||F_o| - \langle|F_o|\rangle|/\Sigma|F_o|$.

Table II. Data Reduction and Refinement Details

	$\mathrm{Ni(\eta^2\text{-}C_6H_4)(Cy_2PCH_2CH_2PCy_2)}$	$\mathrm{\overline{Ni(CH_2CH_2C}_6H_4\text{-}\mathit{o})(Cy_2PCH_2CH_2PCy_2)}$
degradatn correctn	anisotropic[a]	
absorptn correctn	numerical integratn[b]	analytical[c]
transmissn factor range	0.74-0.82	0.72-0.91
scattering factor source	international tables[d] (dispersion corrected)	
hydrogen atom treatment	located by calculation, benzyne hydrogen atom coordinates refined; six group B factors refined—one for each of the groups benzyne, ethyl, and cyclohexyl (4)	located by calculation; three group B factors refined—one for each of the groups arene, ethyl, and *all* cyclohexyl
function minimized by refinement	$\Sigma w(|F_o| - |F_c|)^2$	
w	$\propto[\sigma^2(F_o) + 0.0005F_o^2]^{-1}$	
extinctn correctn[e]	1.69 (16) × 10^{-3}	N/A
no. of reflectns in refinement anal.	4203	2397
R	0.035	0.070
R_w[f]	0.055	0.071
shift/esd ratios	<0.2	<0.2
electron density excursns in final difference map, e Å^{-3}	<±0.5	<±0.5

[a] Method of Churchill and Kalra.[26] [b] SHELX-76 routine.[23] [c] Method of De Meulenaer and Tompa.[27] [d] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 91-101, 149-150. [e] Is x in the empirical expression $F_{corr} = F_c\{1 - (0.0001xF_c^2/\sin\theta)\}$.[23] [f] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$.

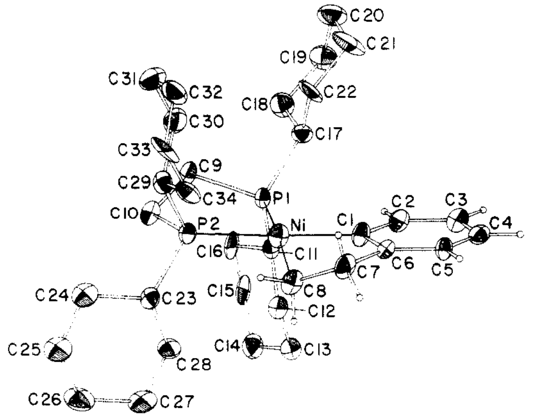

Figure 2. Molecular structure of $\mathrm{\overline{Ni(CH_2CH_2C}_6H_4\text{-}\mathit{o})\text{-}(Cy_2PCH_2CH_2PCy_2)}$. Thermal ellipsoids depict 30% probability surfaces. Methylene and methine hydrogen atoms of the phosphine ligand have been omitted for clarity.

gives the (2-bromophenyl)bromonickel(II) complex 5 which, on treatment with LiCl, gives the corresponding

Scheme I

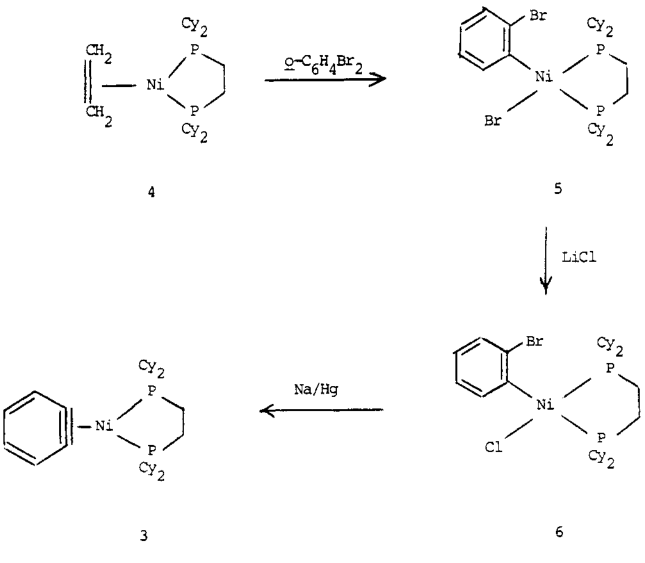

Table III. Selected Bond Lengths and Interbond Angles for $Ni(\eta^2\text{-}C_6H_4)(Cy_2PCH_2CH_2PCy_2)$ (3)

A. Bond Lengths (Å)

Ni–P1	2.140 (1)	C14–C9	1.524 (6)
Ni–P2	2.152 (1)	C15–P1	1.845 (4)
Ni–C1	1.870 (4)	C15–C16	1.522 (6)
Ni–C2	1.868 (4)	C16–C17	1.517 (7)
C1–C2	1.332 (6)	C17–C18	1.514 (8)
C2–C3	1.386 (6)	C18–C19	1.514 (8)
C3–C4	1.383 (7)	C19–C20	1.532 (6)
C3–H3	0.96 (5)	C20–C15	1.532 (6)
C4–C5	1.390 (8)	C21–P2	1.854 (4)
C4–H4	0.93 (5)	C21–C22	1.522 (6)
C5–C6	1.383 (7)	C22–C23	1.525 (7)
C5–H5	1.02 (5)	C23–C24	1.512 (7)
C6–C1	1.389 (6)	C24–C25	1.505 (7)
C6–H6	0.95 (5)	C25–C26	1.532 (7)
C7–P1	1.851 (4)	C26–C21	1.532 (6)
C7–C8	1.533 (6)	C27–P2	1.855 (5)
C8–P2	1.858 (4)	C27–C28	1.496 (7)
C9–P1	1.844 (4)	C28–C29	1.526 (7)
C9–C10	1.539 (6)	C29–C30	1.513 (8)
C10–C11	1.526 (6)	C30–C31	1.466 (9)
C11–C12	1.498 (7)	C31–C32	1.530 (7)
C12–C13	1.519 (8)	C32–C27	1.524 (6)
C13–C14	1.531 (7)		

B. Bond Angles (deg)

P1–Ni–P2	91.8 (1)	C1–C6–H6	125 (3)
P1–Ni–C1	153.9 (1)	P1–C7–C8	111.5 (3)
P1–Ni–C2	112.3 (1)	C7–C8–P2	112.0 (3)
P2–Ni–C1	114.2 (1)	P1–C9–C10	111.1 (3)
P2–Ni–C2	156.0 (1)	P1–C9–C14	112.3 (3)
C1–Ni–C2	41.7 (2)	C10–C9–C14	109.4 (4)
C7–P1–Ni	108.0 (1)	C9–C10–C11	110.6 (4)
C9–P1–Ni	117.5 (1)	C10–C11–C12	111.7 (5)
C15–P1–Ni	117.6 (1)	C11–C12–C13	111.0 (4)
C7–P1–C9	103.9 (2)	C12–C13–C14	111.9 (5)
C7–P1–C15	105.3 (2)	C13–C14–C9	111.2 (4)
C9–P1–C15	103.1 (2)	P1–C15–C16	111.2 (3)
C8–P2–Ni	107.1 (1)	P1–C15–C20	116.6 (3)
C21–P2–Ni	116.3 (1)	C16–C15–C20	110.7 (4)
C27–P2–Ni	117.8 (2)	C15–C16–C17	111.8 (4)
C8–P2–C21	104.8 (2)	C16–C17–C18	110.9 (5)
C8–P2–C27	100.7 (2)	C17–C18–C19	111.3 (4)
C21–P2–C27	108.2 (2)	C18–C19–C20	111.8 (5)
Ni–C1–C2	69.1 (2)	C19–C20–C15	111.2 (4)
Ni–C1–C6	168.6 (4)	P2–C21–C22	110.5 (3)
C2–C1–C6	122.3 (4)	P2–C21–C26	111.5 (3)
Ni–C2–C1	69.2 (3)	C22–C21–C26	109.0 (4)
Ni–C2–C3	167.9 (4)	C21–C22–C23	112.7 (4)
C1–C2–C3	122.9 (4)	C22–C23–C24	110.8 (4)
C2–C3–C4	116.2 (5)	C23–C24–C25	111.5 (4)
C2–C3–H3	127 (3)	C24–C25–C26	111.1 (4)
C4–C3–H3	117 (3)	C25–C26–C21	111.5 (5)
C3–C4–C5	121.0 (5)	P2–C27–C28	115.1 (4)
C3–C4–H4	122 (3)	P2–C27–C32	115.5 (4)
C5–C4–H4	117 (3)	C28–C27–C32	113.4 (4)
C4–C5–C6	121.5 (5)	C27–C28–C29	112.1 (5)
C4–C5–H5	119 (3)	C28–C29–C30	112.6 (5)
C6–C5–H5	120 (3)	C29–C30–C31	113.5 (5)
C5–C6–C1	116.1 (5)	C30–C31–C32	114.2 (5)
C5–C6–H6	119 (3)	C31–C32–C27	111.0 (5)

Table IV. Selected Bond Lengths and Interbond Angles for $\overline{\mathrm{Ni(CH_2CH_2C}}\mathrm{_6H_4}$-*o*)$(Cy_2PCH_2CH_2PCy_2)$ (11)

A. Bond Lengths (Å)

Ni–P1	2.203 (4)	C17–P1	1.85 (1)
Ni–P2	2.170 (4)	C17–C18	1.48 (2)
Ni–C1	1.951 (12)	C18–C19	1.53 (2)
Ni–C8	1.988 (12)	C19–C20	1.49 (2)
C1–C2	1.39 (2)	C20–C21	1.45 (2)
C2–C3	1.38 (2)	C21–C22	1.50 (2)
C3–C4	1.35 (2)	C22–C17	1.49 (2)
C4–C5	1.36 (2)	C23–P2	1.85 (1)
C5–C6	1.38 (2)	C23–C24	1.52 (2)
C6–C1	1.38 (2)	C24–C25	1.52 (2)
C6–C7	1.50 (2)	C25–C26	1.53 (2)
C7–C8	1.46 (2)	C26–C27	1.49 (2)
C9–C10	1.52 (2)	C27–C28	1.49 (2)
C9–P1	1.84 (1)	C28–C23	1.52 (2)
C10–P2	1.84 (1)	C29–P2	1.85 (1)
C11–P1	1.86 (1)	C29–C30	1.49 (2)
C11–C12	1.49 (2)	C30–C31	1.54 (2)
C12–C13	1.50 (2)	C31–C32	1.47 (2)
C13–C14	1.46 (2)	C32–C33	1.41 (2)
C14–C15	1.44 (2)	C33–C34	1.52 (2)
C15–C16	1.50 (2)	C34–C29	1.52 (2)
C16–C11	1.49 (2)		

B. Bond Angles (deg)

P1–Ni–P2	87.7 (1)	P1–C11–C12	113 (1)
P1–Ni–C1	99.8 (4)	P1–C11–C16	119 (1)
P1–Ni–C8	170.7 (4)	C12–C11–C16	112 (1)
P2–Ni–C1	170.7 (4)	C11–C12–C13	114 (1)
P2–Ni–C8	92.7 (4)	C12–C13–C14	115 (1)
C1–Ni–C8	80.9 (5)	C13–C14–C15	114 (1)
C9–P1–Ni	109.0 (4)	C14–C15–C16	116 (2)
C11–P1–Ni	111.1 (5)	C15–C16–C11	114 (1)
C17–P1–Ni	122.2 (4)	P1–C17–C18	118 (1)
C9–P1–C11	106.0 (6)	P1–C17–C22	111 (1)
C9–P1–C17	103.3 (6)	C18–C17–C22	111 (1)
C11–P1–C17	104.0 (6)	C17–C18–C19	111 (1)
C10–P2–Ni	109.9 (4)	C18–C19–C20	112 (1)
C23–P2–Ni	119.6 (4)	C19–C20–C21	111 (1)
C29–P2–Ni	115.9 (4)	C20–C21–C22	115 (1)
C10–P2–C23	103.6 (6)	C21–C22–C17	112 (1)
C10–P2–C29	103.5 (6)	P2–C23–C24	116 (1)
C23–P2–C29	102.4 (6)	P2–C23–C28	112 (1)
Ni–C1–C2	131 (1)	C24–C23–C28	110 (1)
Ni–C1–C6	115 (1)	C23–C24–C25	112 (1)
C2–C1–C6	114 (1)	C24–C25–C26	110 (1)
C1–C2–C3	123 (1)	C25–C26–C27	112 (1)
C2–C3–C4	120 (1)	C26–C27–C28	113 (1)
C3–C4–C5	120 (1)	C27–C28–C23	112 (1)
C4–C5–C6	118 (1)	P2–C29–C30	115 (1)
C5–C6–C1	125 (1)	P2–C29–C34	113 (1)
C5–C6–C7	121 (1)	C30–C29–C34	105 (1)
C1–C6–C7	114 (1)	C29–C30–C31	113 (1)
C6–C7–C8	108 (1)	C30–C31–C32	111 (1)
C7–C8–Ni	111 (1)	C31–C32–C33	112 (2)
P1–C9–C10	110 (1)	C32–C33–C34	112 (1)
C9–C10–P2	111 (1)	C33–C34–C29	113 (1)

(2-bromophenyl)chloronickel(II) complex **6**.[28] The latter is reduced by sodium amalgam in THF to give, after recrystallization from cyclohexane/hexane, yellow microcrystals of empirical formula $Ni(C_6H_4)(Cy_2PCH_2CH_2PCy_2)$ in 72% isolated yield (Scheme I). Powdered lithium and sodium also rapidly reduce **6** to **3**, but it has proved impossible to obtain a pure product with these metals owing to further reaction leading to decomposition.

The isolated solid is air-stable for a short period, but solutions in organic solvents are very air-sensitive. The 70-eV mass spectrum shows a prominent parent ion peak at *m*/*z* 556 and cryoscopic measurements in benzene confirm that the complex is monomeric. The formulation as a η^2-benzyne complex (**3**) rests securely on the single-crystal X-ray diffraction study (see below) and is supported by spectroscopic data. The $^1H\{^{31}P\}$ NMR spectrum shows an AA′BB′ pattern in the usual aromatic region, and there is a singlet in the $^{31}P\{^1H\}$ NMR spectrum due to equivalent phosphorus atoms. Of the three aromatic resonances in the $^{13}C\{^1H\}$ NMR spectrum, only one, at δ 145.4, is unaffected by off-resonance decoupling, and it must therefore be due to the two coordinated benzyne carbon atoms. It consists of a symmetrical five-line multiplet, the second

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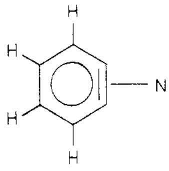
[28] Miller et al.[18] have reported that attempted chromatography of *trans*-$NiBr(C_6H_4Br\text{-}2)(PEt_3)_2$ on acidic alumina gives quantitatively *trans*-$NiCl(C_6H_4Br\text{-}2)(PEt_3)_2$ owing to exchange with chloride ion on the alumina. We observed mixtures of **5** and **6** when **5** was chromatographed, so it was convenient to convert **5** completely into **6**.

and fourth lines being more intense than the other three. The appearance is typical of one half of an AA′XX′ pattern, the sum of the two P–C coupling constants being 54 Hz. A similar pattern is observed in the ^{13}C NMR spectrum of Pt(PhC$_2$Ph)(PPh$_3$)$_2$, where $^2J_{PC} + {}^2J_{PC'}$ is 61 Hz.[29] This observation shows that rotation of the benzyne ligand about the metal–alkyne bond is slow on the NMR time scale at room temperature, as is true also for coordinated alkynes in Pt(alkyne)(PPh$_3$)$_2$ complexes.[30,31] If rotation were fast, a simple doublet with a separation corresponding to J_{PC} (average) would be observed. In contrast, $\Delta G^{\ddagger}$ for the corresponding rotation in Ta(η-C$_5$Me$_5$)Me$_2$(η^2-C$_6$H$_4$) (1) has been estimated as $\leq$9 kcal mol^{-1}.[3]

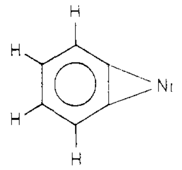
The IR spectrum of **3** shows a characteristic strong, sharp band at 1583 cm^{-1} (KBr disk) which we assign tentatively to the "ν(C≡C)" vibration of benzyne modified by coordination, cf. ca. 1700 cm^{-1} for alkyne complexes of Ni(0) and Pt(0).[32] The lower value for **3** may reflect the fact that its "C≡C" distance is longer than those observed in typical alkyne complexes of Ni(0) and Pt(0) (see below). Since ν(C≡C) for matrix-isolated benzyne is 2085 cm^{-1},[33] the value of $\Delta\nu$(C≡C) ($\nu_{\text{ligand}} - \nu_{\text{complex}}$) for **3** is ca. 500 cm^{-1}, which is approximately equal to that found for M(alkyne)L$_2$ complexes. Although the possibility that other aromatic ring C–C stretching vibrations contribute to the 1583 cm^{-1} absorption cannot be excluded, our assignment is supported by the fact that the IR spectrum of the μ-*o*-phenylene complex Ir$_2$(η-C$_5$Me$_5$)$_2$(μ-C$_6$H$_4$)(CO)$_2$ shows only a typical aromatic C–C stretching band at 1554 cm^{-1}.[34]

Structure of Ni(η^2-C$_6$H$_4$)(Cy$_2$PCH$_2$CH$_2$PCy$_2$) (3). The molecular geometry is shown in Figure 1, and bond lengths and interbond angles are in Table III. The molecule consists of a central nickel atom coordinated by a symmetric η^2-benzyne [Ni–C1 = 1.870 (4) Å; Ni–C2 = 1.868(4) Å] and the bidentate di(tertiary phosphine) [Ni–P1 = 2.140 (1) Å; Ni–P2 = 2.152 (1) Å]. The coordination geometry is close to trigonal planar, characteristic of alkene and alkyne complexes of Ni(0), Pd(0), and Pt(0).[35] The Ni–C distances are similar to those observed in the diphenylacetylene complex Ni(PhC$_2$Ph)(CN-*t*-Bu)$_2$[36] and are ca. 0.1 Å shorter than those found in analogous nickel(0)–olefin complexes, e.g., 1.981 (2) Å (average) in Ni(Me$_2$C=CMe$_2$)(Cy$_2$PCH$_2$CH$_2$PCy$_2$).[37] The Ni–P distances in **3** are very close to those observed in the latter compound. The benzyne ligand is planar to within experimental error, with maximum out-of-plane deviations for carbon and hydrogen atoms of 0.004 (3) and 0.07 (3) Å, respectively. The nickel atom and the phosphorus atoms are each displaced slightly to one side of the benzyne plane, the maximum displacement being 0.133 (1) Å (for P1).

The C1–C2 bond length of 1.332 (6) Å is close to the value for an uncoordinated double bond and is significantly longer than the value of 1.25–1.30 Å commonly observed in M(alkyne)L$_2$ (M = Ni, Pt) complexes,[35] e.g., 1.284 (16) Å in Ni(PhC$_2$Ph)(CN-*t*-Bu)$_2$[36] and 1.297 (8) Å in Pt(cyclohexyne)(PPh$_3$)$_2$.[38] The remaining five C–C bond distances in the six-membered ring are almost identical (average 1.385 Å) and are similar to the bond lengths in benzene itself. These features are consistent with delocalized aromatic structures for the benzyne ligand such as I and II, and they imply that **3** could be described as a benzonickelacyclopropene.



I



II

It may be significant that the C1–C2 distance of 1.364 (5) Å in the tantalum complex Ta(η-C$_5$Me$_5$)Me$_2$(η^2-C$_6$H$_4$) (**1**) is even longer than that in **3** and that, in contrast with **3**, the remaining ring C–C distances in **1** show a slight, but distinct, alternation (average 1.367 ± 0.007 Å, 1.407 ± 0.007 Å).[3,4] If benzyne is assumed to donate two electrons to a neutral metal atom, then **1** is a 14e complex and is more unsaturated than **3**, which is a 16e complex. The differences noted above may reflect the fact that in **1** both pairs of filled orthogonal π-orbitals of benzyne are used in bonding to tantalum, so that conjugation with the aromatic π-orbitals is reduced. There is good evidence that alkynes can donate more than two electrons, especially in their complexes with early transition elements that have relatively few d electrons.[39]

Reactivity of 3. As expected for a low-valent d^{10} metal complex, **3** reacts readily with electrophiles. The benzyne ring is completely removed as benzene by the action of trifluoroacetic acid in THF, the inorganic product being Ni(O$_2$CCF$_3$)$_2$(Cy$_2$PCH$_2$CH$_2$PCy$_2$). Addition of iodine (1 equiv) to **3** in THF at −30 °C gives the 2-iodophenyl complex NiI(C$_6$H$_4$I-2)(Cy$_2$PCH$_2$CH$_2$PCy$_2$) (**7**) in ca. 95% yield, as estimated from the ^{31}P{^{1}H} NMR spectrum of the reaction mixture. The product is spectroscopically identical with that obtained by oxidative addition of *o*-diiodobenzene to the ethylene complex **4**. The reaction of **3** with neat, dry methyl iodide is complete within ca. 30 min at 25 °C and, after evaporation of the methyl iodide, gives an orange crystalline mixture containing predominantly (ca. 95%) the *o*-tolylnickel(II) complex NiI(C$_6$H$_4$Me-2)(Cy$_2$PCH$_2$CH$_2$PCy$_2$) (**8**), together with ca. 5% of the phenyl analogue NiI(C$_6$H$_5$)(Cy$_2$PCH$_2$CH$_2$PCy$_2$) (**9**). Both compounds were identified by comparison with samples prepared independently from **4**: the first by oxidative addition of 2-bromotoluene and subsequent reaction of the resulting bromo *o*-tolyl complex with NaI; the second by oxidative addition of iodobenzene. The ^{31}P{^{1}H} NMR spectra of complexes **7**–**9** consist of an AB quartet with a coupling constant of ca. 20 Hz, indicative of mutually cis, inequivalent phosphorus atoms.

The insertion reactions of **3** with iodine and methyl iodide are similar to those reported for the (cyclohexyne)- and (cycloheptyne)platinum(0) complexes Pt(cyclic alkyne)L$_2$ (L$_2$ = 2PPh$_3$, Ph$_2$PCH$_2$CH$_2$PPh$_2$).[40] In the reaction of methyl iodide with Pt(C$_6$H$_8$)(PPh$_3$)$_2$, an intermediate platinum(II) complex, PtI(Me)(C$_6$H$_8$)(PPh$_3$)$_2$, formed by oxidative addition to the metal, was isolated and shown to isomerize to the final insertion product PtI(C$_6$H$_8$Me-2)(PPh$_3$)$_2$.[40] The corresponding reactions of **3** probably

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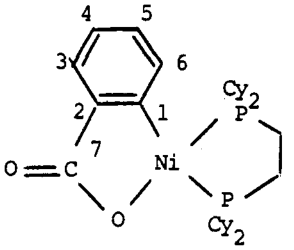
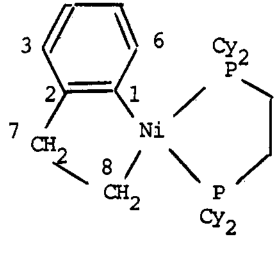
proceed similarly, although there was no evidence for oxidative addition intermediates.

A solution of **3** in THF rapidly absorbs CO_2 (1 mol/mol of **3**) to give almost quantitatively the yellow 2-carboxyphenyl insertion product $\overline{Ni(C_6H_4COO)}$-$(Cy_2PCH_2CH_2PCy_2)$ (**10**). The proposed structure is supported by the IR spectrum, which shows strong ν(OCO) absorptions at 1636 and 1622 cm^{-1} (cf. 1660 and 1620 cm^{-1} for $(\eta\text{-}C_5H_5)_2\overline{Ti(C_6H_4COO)}$).[12] The $^{13}C\{^1H\}$ NMR spectrum contains seven high frequency signals, of which three are unaffected by off-resonance decoupling. They are a singlet at δ 144.3 due to C^2, the carbon atom attached to the carboxyl carbon atom, a multiplet at δ 154.4 due to C^1, which is σ-bonded to nickel, and a doublet at δ 182.5 due to the carboxyl carbon atom C^7. The $^{31}P\{^1H\}$ NMR spectrum shows the expected AB quartet with a coupling of ca. 20 Hz. Reaction of **10** with CF_3CO_2H (2 equiv) in dichloromethane gives $Ni(O_2CCF_3)_2(Cy_2PCH_2CH_2PCy_2)$ quantitatively, and benzoic acid can be isolated in 65% yield after vacuum sublimation. In view of the ready formation of **10** from **3**, the failure to isolate a (benzyne)platinum(0) complex by elimination of CO_2 from $\overline{Pt(C_6H_4COO)}(PPh_3)_2$[15b] is not surprising.



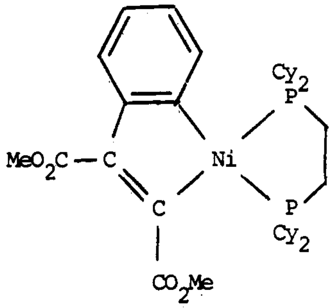
10

Complex **3** dissolved in cyclohexane reacts with ethylene (3 atm) at 80 °C to give yellow plates of a 1:1 adduct in ca. 50% yield. The 70-eV mass spectrum shows a parent ion peak, and the ^1H NMR spectrum shows a two proton multiplet at δ 3.60 due to one of the added methylene groups. The signal due to the other pair of methylene protons is probably masked by the CH_2 and C_6H_{11} resonances of the di(tertiary phosphine). The methylene ^{13}C NMR resonances also could not be observed, although a doublet at δ 163.7 and a multiplet at δ 169.4 can be assigned to the aromatic carbon atoms adjacent to a CH_2 group and to the nickel atom, respectively, in the metallacyclic structure **11**. In agreement with this formulation, the $^{31}P\{^1H\}$ NMR spectrum shows the phosphorus atoms to be inequivalent, whereas in the alternative tetrahedrally coordinated structure containing $\eta^2\text{-}C_6H_4$ and $\eta^2\text{-}C_2H_4$ they would have been equivalent. The nickelaindan structure **11** has been confirmed by a single-crystal X-ray analysis (see below).



11

Dimethyl acetylenedicarboxylate reacts immediately with **3** at −10 °C to give the orange nickelaindan insertion product **12** almost quantitatively. The IR spectrum contains intense ester and C=C absorptions at 1710 and 1533 cm^{-1}, respectively, and the ^1H and $^{13}C\{^1H\}$ NMR spectra both show two equally intense singlets due to inequivalent CO_2Me groups. The other peaks in the ^{13}C NMR spectrum (see Experimental) can also be satisfactorily assigned on the basis of structure **12**, and the $^{31}P\{^1H\}$ NMR spectrum shows the expected AB quartet.



12

The formation of **10**–**12** by insertion of unsaturated molecules into the nickel–benzyne bond is clearly analogous to the formation of metallacycles from the presumed benzyne complexes $(\eta\text{-}C_5H_5)_2M(\eta^2\text{-}C_6H_4)$ (M = Ti, Zr)[10,13] (see Introduction). To the extent that **3** can be regarded as a benzonickelacyclopropene, these insertions are also similar to those recently reported for certain phenyl- and methylnickel(II) complexes.[41,42] Surprisingly, however, **3** does not undergo insertion with diphenylacetylene to give the expected 2,3-diphenyl-1-nickelaindene. In a slow reaction (8 h, 80 °C), the only compound that could be isolated, in 60% yield, was the diphenylacetylene complex $Ni(PhC{\equiv}CPh)(Cy_2PCH_2CH_2PCy_2)$ (**13**), which was also obtained by displacement of ethylene from **4** with diphenylacetylene. The fate of the displaced benzyne has not been established. Attempts to induce insertion of diphenylacetylene into the nickel–benzyne bond of **3** at higher temperatures led only to hexaphenylbenzene, as a result of catalytic cyclotrimerization of diphenylacetylene. This failure to insert is in contrast with the behavior of the presumed $(\eta\text{-}C_5H_5)_2M(\eta^2\text{-}C_6H_4)$ (M = Ti, Zr) complexes and may be a consequence of steric hindrance by the bulky cyclohexyl groups to the approach of the ligand.

Benzyne is also lost when **3** is stirred under nitrogen (80 atm) for 3 days at 20 °C. Deep violet crystals admixed with brown crystals that contain neither nitrogen nor aromatic groups are obtained. Complex **3** also reacts immediately with CO (1 atm) at room temperature to give species containing terminal and ketonic carbonyl groups. These and other reactions are being examined.

Structure of $\overline{Ni(CH_2CH_2C_6H_4\text{-}o)}(Cy_2PCH_2CH_2PCy_2)$ (11). The molecular stereochemistry is shown in Figure 2; bond lengths and interbond angles are in Table

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IV. The complex is a nickelaindan having a half-chair-shaped five-membered ring. The coordination arrangement about the nickel atom is essentially square planar, but there is a small tetrahedral distortion (average out-of-plane deviation = 0.14 Å).[43] The aromatic ring, which is planar to within experimental error, is both twisted about Ni–C1 and bent out of the coordination "plane". Atom deviations are listed in ref 43. The Ni–C8 bond length in **11** [1.988 (12) Å] falls in the range 1.94–1.99 Å found for various nickel(II) alkyls, e.g., $\overline{\mathrm{Ni(bpy)(CH_2)_3CH_2}}$ [1.949 (4) Å],[44] NiMe(acac)(PCy_3) [1.94 (1) Å],[45] and NiEt(acac)(PPh_3) [1.97 (1) Å],[44] whereas the Ni–C1 distance in **11** [1.951 (12) Å] is significantly longer than the corresponding nickel(II)–aryl distance in Ni(C_6H_5)(η-C_5H_5)(PPh_3),[47] probably because of the presence of the trans phosphine ligand. The Ni–P distances [Ni–P1 = 2.203 (4) Å; Ni–P2 = 2.170 (4) Å] are unexceptional [cf., e.g., 2.159 Å in NiMe(acac)(PCy_3)].[45]

Conclusion

The alkali-metal reduction of a (2-bromophenyl)nickel(II) halide complex, a method first employed by Miller et al.,[18] has afforded Ni(η^2-C_6H_4)($Cy_2PCH_2CH_2PCy_2$) (**3**), the first well-defined mononuclear η^2-benzyne complex of a d^{10} element and, after Ta(η-C_5Me_5)Me_2(η^2-C_6H_4) (**1**), only the second structurally characterized mononuclear η^2-C_6H_4 complex of any element. Like most of the methods used to form metal complexes of short-lived unsaturated fragments (e.g., cyclobutadiene,[48] carbenes,[49,50] and *o*-xylene[51,52]), the synthesis does not produce "free" benzyne at any stage but instead generates benzyne on the metal center. Provided the appropriate (2-halophenyl)metal precursors can be made, it should be possible to synthesize and determine the structures of benzyne complexes of other transition elements. It will be particularly interesting to see whether the lengths of the uncoordinated C–C bonds in the benzyne ring in such complexes are essentially equal, as in **3** or, alternate, as in **1**. This should provide a test of the hypothesis that bond alternation is associated with donation of more than two electrons from the benzyne ring to the metal atom.

The bulky bidentate ligand $Cy_2PCH_2CH_2PCy_2$ undoubtedly imparts chemical and thermal stability to the nickel(0)–benzyne system as a consequence of its strong electron-donating ability, which enhances π-back-bonding to the unsaturated fragment, combined with its ability to shield the metal from attacking molecules. We have recently found that a stable complex Ni(η^2-C_6H_4)$(PCy_3)_2$, containing the bulky monodentate ligand tricyclohexylphosphine, can be made similarly to **3**. It is less certain that bulky ligands are *required* to stabilize η^2-benzyne relative to μ-*o*-phenylene coordination, i.e., **3** rather than **2**. Studies on C_6H_4Ni complexes containing sterically less demanding monodentate and bidentate ligands, including 2,2′-bipyridyl, trimethylphosphine, and 1,2-bis(dimethylphosphino)ethane, are clearly warranted. Such complexes can be expected to undergo insertion under mild conditions with an even wider range of substrates than does **3**.

Registry No. **3**, 97921-18-1; **4**, 91513-98-3; **5**, 97921-23-8; **6**, 97921-16-9; **7**, 97921-15-8; **8**, 97921-14-7; **9**, 97921-12-5; **10**, 97921-20-5; **11**, 97921-21-6; **12**, 97921-22-7; **13**, 97921-17-0; $NiCl_2$($Cy_2PCH_2CH_2PCy_2$), 96555-88-3; Ni $(O2CCF3)_2$-(Cy2PCH2CH2PCy2), 97921-11-4; NiBr(C6H4Me-2)-(Cy2PCH2CH2PCy2), 97921-13-6; NiI2(Cy2PCH2CH2PCy2), 97921-19-2; *o*-C6H4Br2, 583-53-9; ethylene, 74-85-1; iodobenzene, 591-50-4; *o*-bromotoluene, 95-46-5; *o*-diiodobenzene, 615-42-9; diphenylacetylene, 501-65-5; dimethyl actylenedicarboxylate, 762-42-5.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters (anisotropic for non-hydrogen atoms, isotropic for hydrogen atoms), and observed and calculated structure factors for Ni(η^2-C_6H_4)($Cy_2PCH_2CH_2PCy_2$) (**3**) and $\overline{\mathrm{Ni(CH_2CH_2C_6H_4}}$-*o*)($Cy_2PCH_2CH_2PCy_2$) (**11**) (51 pages). Ordering information is given on any current masthead page.

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[43] Atom deviations (Å) from the best plane through the set Ni, C(1), C(8), P(1), and P(2) are as follows: Ni, –0.003 (1); C(1), –0.193 (9); C(8), 0.310 (9); P(1), 0.011 (2); P(2), –0.007 (2).

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