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Synthesis and Characterization of Bis(phosphine)nickel(0) Complexes Containing Nonsymmetrically Substituted Acetylenes

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Some new nickel π-complexes of the general formula $L_2Ni(XC{\equiv}CY)$ (L = PCy_3, PPh_3, $P(O\text{-}o\text{-}Tol)_3$; X = Ph, Me; Y = Me, Et, *i*-Pr, *t*-Bu, H, $SiMe_3$, $SiPh_3$) were prepared, and the influence of various substituents and ligands on the properties of the π-bond, three-membered metallacycle was investigated. With X = Ph kept constant, the following substituent variations of Y have been tested Y = Me, Et, *i*-Pr, *t*-Bu (systematic α-methyl perturbation on the tetrahedral C atom), H, $SiMe_3$, and $SiPh_3$. It could be established that the quaternary C atoms of the three-membered metal ring system have very different electron densities (^{13}C NMR analysis) that are caused by nonsymmetrical substitution. The strongest polarization of the acetylene bond between the sp carbon atoms could be obtained with X = Ph, Y = $SiMe_3$ and X = Ph, Y = $SiPh_3$ substituted acetylenes. The differences between the interaction of these C atoms with the metal center have been confirmed by an X-ray diffraction study of the $(PPh_3)_2Ni(PhC^1{\equiv}C^2SiMe_3)$ complex: monoclinic, space group $P2_1/c$; $a = 12.200\ (2)$ Å, $b = 12.564\ (2)$ Å, $c = 26.607\ (4)$ Å, $\alpha = 90°$, $\beta = 98.37\ (1)°$, $\gamma = 90°$, $V = 4034.8\ (1.1)$ Å^3, $Z = 4$, $R = 0.0477$; Ni–C^1 and Ni–C^2 bond lengths 1.884 (6) and 1.926 (6) Å; bend-back angles 31.8 (5)° (on C^1) and 41.3 (5)° (on C^2). The electron density of the complexed acetylene carbon atoms is influenced also by the properties of phosphine ligands on the transition metal. Donor phosphine ligands like PCy_3 caused an increase, while acceptor ones like $P(O\text{-}o\text{-}Tol)_3$ caused a decrease in polarization between the two C atoms of the metallacycle.

Introduction

Much of the current interest has been devoted to unsaturated organic substrates coordinated to transition metals because of their importance in organic synthesis.[2] Several catalytic processes are known where the presence of nickel promotes the reactivity of the acetylene triple bond. Among these are the carbonylation reaction of acetylene to acrylic acid (Reppe),[3] the cyclooligomerization of acetylene (COT synthesis),[4] and the cooligomerization of butadiene and acetylene to provide a wide variety of products.[5] In order to help the understanding of the mechanisms of these reactions, we initiated a study of some transition-metal triple-bond π-systems. The fundamental idea of our investigations was the assumption that the reactivity of such complexes is strongly influenced by introducing some kind of nonsymmetry into the metal ring system. We prepared therefore several new acetylene nickel(0) complexes using systematically substituted nonsymmetrical acetylenes and determined how various parameters influence the behavior of the three-membered carbon–nickel π-system.

In this paper we present our results based on spectroscopic and X-ray data of complexes of the type $(PR_3)_2Ni(XC{\equiv}CY)$ (R = Cy, Ph, O-*o*-Tol; X = Ph, Me; Y = Me, Et, *i*-Pr, *t*-Bu, H, $SiMe_3$, $SiPh_3$).

Experimental Section

General Considerations. All reactions and manipulations were performed under a prepurified argon atmosphere using Schlenk line techniques. Solvents were dried and deoxygenated by distillation over sodium/benzophenone or sodium/potassium alloy under argon just prior to use.

Starting Materials. The complexes $Ni(COD)_2$[6] and $(PPh_3)_2Ni(C_2H_4)$[7] and the PR_3 ligands (R = Cy,[8] O-*o*-Tol[9]) were prepared by literature methods. The acetylenes PhC_2H, PhC_2Ph, and MeC_2SiMe_3 were purchased from commercial suppliers and used without further purification, while PhC_2Me,[10] PhC_2Et,[11] PhC_2-*i*-Pr,[12] PhC_2-*t*-Bu,[13] PhC_2SiMe_3,[14] and PhC_2SiPh_3[15] were prepared by literature methods and checked by GC–MS and IR and NMR spectroscopy (see Table I).

Physical Measurements. NMR spectra, in THF-d_8 solution, were recorded at 21 °C using a Bruker AMX-300T spectrometer equipped with a 5-mm QNP probe. Interpretations and assignments of ^{13}C NMR spectra were supported by using DEPT techniques for protonated and quaternary-only sequence for quaternary carbon atoms.[16] The signals of the complexed

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Table I. Spectroscopic Characterization of the Acetylenes Used[a]

$XC^1{\equiv}C^2Y$		IR	^1H NMR δ, ppm		
			$X = C_6H_5$		
X	Y	$\nu_{max}(C{\equiv}C)$, cm^{-1}	H_o[b]	H_{m+p}	Y
Ph	Ph	2223.0[19]	7.49–7.53 (m, 4 H)	7.37–7.39 (m, 6 H)	
Ph	Me	2250.2	7.35–7.39 (m, 2 H)	7.25–7.27 (m, 3 H)	2.00 (s, 3 H, 1 CH_3)
Ph	Et	2236.5	7.36–7.45 (m, 2 H)	7.25–7.27 (m, 3 H)	1.21 (t, 3 H, 1 CH_3, $^3J(HH)$ = 7.5 Hz) 2.40 (q, 2 H, 1 CH_2, $^3J(HH)$ = 7.5 Hz)
Ph	*i*-Pr	2230.3	7.30–7.35 (m, 2 H)	7.23–7.30 (m, 3 H)	1.24 (d, 3 H, 1 CH_3, $^3J(HH)$ = 6.8 Hz) 2.79 (hp, 1 H, 1 CH, $^3J(HH)$ = 6.4 Hz)
Ph	*t*-Bu	2237.4	7.30–7.36 (m, 2 H)	7.20–7.30 (m, 3 H)	1.31 (s, 9 H, 1 CMe_3)
Ph	H	2109.2	7.43–7.47 (m, 2 H)	7.29–7.34 (m, 3 H)	3.53 (s, 1 H)
Ph	$SiMe_3$	2159.0	7.37–7.40 (m, 2 H)	7.25–7.27 (m, 3 H)	0.20 (s, 9 H, 1 $SiMe_3$)
Ph	$SiPh_3$	2160.0		7.35–7.73 (m, 20 H, C_6H_5 and $SiPh_3$)	
Me	$SiMe_3$	2182.9	1.00 (s, 3 H, 1 CH_3)		0.09 (s, 9 H, 1 $SiMe_3$)

$XC^1{\equiv}C^2Y$		^{13}C NMR δ, ppm						
		$X = C_6H_5$						
X	Y	C_{ipso}	C_o[c]	C_m	C_p	C^1	C^2	Y
Ph	Ph	124.21	132.18	129.09	128.90	89.92		
Ph	Me	125.17	132.05	128.83	128.06	80.27[d]	86.05[d]	3.79 (s, 1 C, 1 CH_3)
Ph	Et	125.11	132.09	128.83	128.09	80.71[d]	91.90[d]	14.27 (s, 1 C, 1 CH_3) 13.45 (s, 1 C, 1 CH_2)
Ph	*i*-Pr	125.00	132.08	128.78	128.08	80.53	95.81	23.33 (s, 2 C, 2 CH_3) 21.84 (s, 1 C, 1 CH)
Ph	*t*-Bu	125.01	132.04	128.73	128.03	79.99	98.47	31.25 (s, 3 C, 1 CMe_3) 28.50 (s, 1 C, 1 CMe_3)
Ph	H	123.45	132.63	129.01	129.26	84.08	78.67	
Ph	$SiMe_3$	124.10	132.46	128.92	129.20	105.99	94.00	−0.07 (s, 3 C, 1 $SiMe_3$)
Ph	$SiPh_3$	123.53	130.59	128.65	129.08	110.43	89.63	
		134.46	136.24	132.86	129.87	($SiPh_3$)		
Me	$SiMe_3$					103.38[d]	83.58[d]	4.29 (s, 1 C, 1 CH_3) 0.13 (s, 3 C, 1 $SiMe_3$)

[a] Key: s, singlet, d, doublet; t, triplet; q, quartet; hp, heptet; m, multiplet. [b] H_o, H_m, and H_p are the ortho, meta, and paraprotons of C_6H_5. [c] C_o, C_m, and C_p are the ortho, meta, and para carbon atoms of C_6H_5. [d] Assignment of quaternary C atoms by ^1H NMR coupled spectra.

acetylene carbon atoms are shifted to the region of the C atoms of all aromatic signals of our Ni(0) complexes (see Figure 1); consequently, the quaternary-only sequence was necessary. WALTZ16[17] decoupling was applied. The total acquisition time for the ^{13}C NMR spectra varied between 1 and 16 h. The measured digital resolution was 0.21 Hz for ^1H and 0.67 Hz for ^{13}C NMR spectroscopy. Peak positions are referenced to THF, THF-d_8 solvent. Shifts of ^{31}P NMR spectra are relative to external 85% H_3PO_4, with downfield values reported as positive. Infrared spectra (0.2-mm matched sodium chloride cells; THF solutions) were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer. GC–MS data were obtained on a Jeol B 300 GC–MS spectrometer. Elemental analyses were performed by the Microanalytical Laboratory at the University of Veszprém. Melting points were determined in sealed capillaries. Key to NMR data: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, double doublet (ABX/AMX system); a symmetrical doublet due to coupling with the trans phosphorus and each resonance appeared to be further split into a symmetrical doublet due to coupling with the cis phosphorus.[20]

Syntheses. General pathways to prepare acetylene nickel(0) complexes are well-known.[18] Methods A and B were applied.

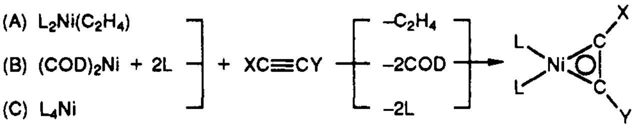

Table II. Amount of Starting Compounds for Methods A and B

Method A (1.5 mmol of Acetylene)

XC≡CY			XC≡CY		
X	Y	amt, g	X	Y	amt, g
Ph	Ph	0.267	Ph	H	0.153
Ph	Me	0.174	Ph	$SiMe_3$	0.261
Ph	Et	0.195	Ph	$SiPh_3$	0.541
Ph	*i*-Pr	0.216	Me	$SiMe_3$	0.168
Ph	*t*-Bu	0.237			

Method B (10 mmol of PR_3 and 5 mmol of Acetylene)

		XC≡CY		
PR_3	amt, g	X	Y	amt, g
PCy_3	2.804	Ph	$SiMe_3$	0.871
P(O-*o*-Tol)$_3$	3.52	Ph	$SiMe_3$	0.871
PCy_3	2.804	Me	$SiMe_3$	0.561
P(O-*o*-Tol)$_3$	3.52	Me	$SiMe_3$	0.561

Method A. A 1.5-mmol sample of the appropriate acetylene (see Table II) was slowly added at room temperature to a THF solution (15 mL) of 1.5 mmol (0.917 g) of $(PPh_3)_2Ni(C_2H_4)$. After the yellow-brownish solution was stirred at 25 °C for 30 min, the mixture was heated to 40–50 °C. When the steady evolution of gas stopped, the solution was filtered and 5 mL of *n*-hexane was added. By cooling the mixture to −40 or −78 °C, crystallization could be observed after 2–5 days. The crystalline compounds were then collected by filtration, washed twice with cold *n*-hexane, and dried in vacuo. The color and yield of the complexes are reported in the following section.

Method B. A 10-mmol amount of phosphine was added at room temperature to a solution of 5 mmol (1.375 g) of $Ni(COD)_2$ in 50 mL of toluene; then 5 mmol of the appropriate acetylene (see Table II) was slowly added dropwise to this dark brown mixture at 0 °C. The reaction solution was kept at this temperature for 30 min, and the solvent was removed under reduced

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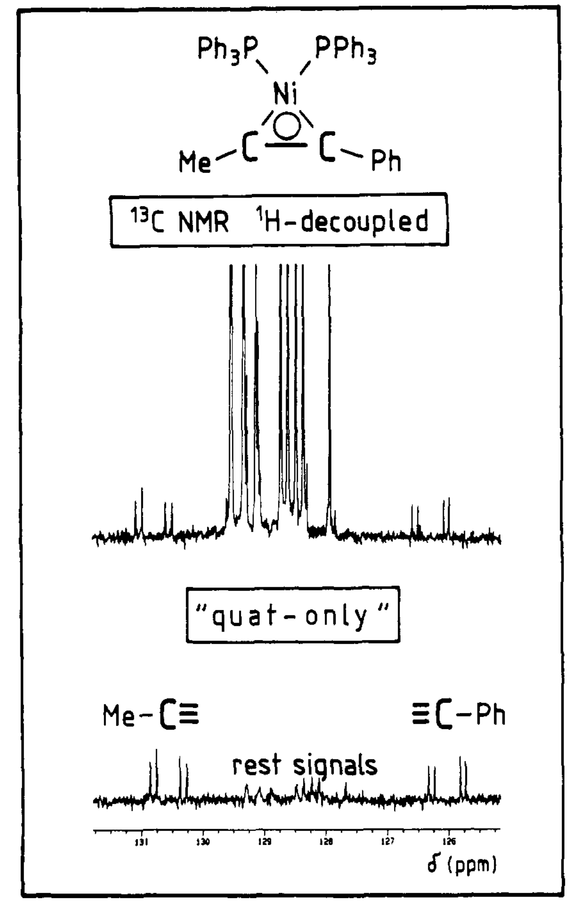

Figure 1. Assignment of the chemical shifts of the acetylene C atoms in the (PPh$_3$)$_2$Ni(PhC$\equiv$CMe) complex by the "quaternary-only" sequence.

pressure. Recrystallization of the residue from *n*-hexane or toluene/ether solution at −78 °C (in the course of 2 days) provided analytically pure substances.

(PPh$_3$)$_2$Ni(PhC$\equiv$CPh)[19-21] **(1).** Method A (yellow microcrystals, 82%): mp 119 °C dec; ^{1}H NMR δ 6.75 (m, 10 H, 2 C$_6$H$_5$), 6.99–7.80 (m, 30 H, 2 PPh$_3$); ^{13}C NMR δ 124.19 (s, C^1 and C^2), 124.58, 127.55–129.26, 132.16–132.73, 134.20–135.09, 135.72, 136.39–137.2 (m, 48 C, 2 C$_6$H$_5$ and 2 PPh$_3$) (An exact assignment of all aromatic C signals was not attempted because of the higher order of the spectra of all complexes); ^{31}P NMR δ 40.03; IR ν_{max}(C$\equiv$C) 1787 cm^{-1}. Anal. Calcd for C$_{50}$H$_{40}$Ni$_1$P$_2$ (761.52): C, 78.86; H, 5.29; Ni, 7.72; P, 8.13. Found: C, 78.82; H, 5.33; Ni, 7.71; P, 8.15.

(PPh$_3$)$_2$Ni(PhC$\equiv$CMe)[20] **(2).** Method A (yellow needles, 80%): mp 155 °C dec; ^{1}H NMR δ 1.74 (dd, 3 H, 1 CH$_3$, ^{4}J(PH) = 4.5, 1 Hz), 6.71–6.77 (m, 5 H, 1 C$_6$H$_5$), 6.79–7.69 (m, 30 H, 2 PPh$_3$); ^{13}C NMR δ 11.41 (dd, 1 C, 1 CH$_3$, ^{3}J(PC) = 12, 4.5 Hz), 126.03 (dd, C^1, ^{2}J(PC) = 38.82, 6.9 Hz) [XC^1$\equiv$C^{2}Y (X = Ph, Me; Y = Me, Et, *i*-Pr, *t*-Bu, H, SiMe$_3$, SiPh$_3$)], 130.57 (dd, C^2, ^{2}J(PC) = 36.88, 8.25 Hz), 124.11, 127.69–129.31, 132.04–132.73, 134.37–134.70, 136.3–137.86 (m, 42 C, 1 C$_6$H$_5$ and 2 PPh$_3$); ^{31}P NMR δ 40.39, 41.47 (^{2}J(PP) = 27.1 Hz) (AB/AX system for the phosphorus atoms); IR ν_{max}(C$\equiv$C) 1819.4 cm^{-1}. Anal. Calcd for C$_{45}$H$_{38}$Ni$_1$P$_2$ (699.75): C, 77.27; H, 5.48; Ni, 8.39; P, 8.86. Found: C, 76.98; H, 5.42; Ni, 8.37; P, 8.92.

(PPh$_3$)$_2$Ni(PhC$\equiv$CEt) (3). Method A (yellow needles, 85%): mp 156 °C; ^{1}H NMR δ 0.88 (t, 3 H, 1 CH$_3$, ^{3}J(HH) = 6.9 Hz), 2.09 (q, 2 H, 1 CH$_2$, ^{3}J(HH) = 6.9 Hz), 6.74 (m, 5 H, 1 C$_6$H$_5$), 6.98–7.70 (m, 30 H, 2 PPh$_3$); ^{13}C NMR δ 14.99 (d, 1 C, 1 CH$_3$, ^{4}J(PC) = 11.9 Hz), 22.81 (dd, 1 C, 1 CH$_2$, ^{3}J(PC) = 11.2, 4.7 Hz), 127.21 (dd, C^1, ^{2}J(PC) = 36.5, 6.5 Hz), 134.9 (dd, C^2, ^{2}J(PC) = 36.1, 8.07 Hz), 123.77, 127.56–129.31, 132.07–132.73, 134.34–134.98, 135.7, 136.94–138.08 (m, 42 C, 1 C$_6$H$_5$ and 2 PPh$_3$); ^{31}P NMR δ 40.14, 40.99 (^{2}J(PP) = 28.43 Hz); IR ν_{max}(C$\equiv$C) 1824.3 cm^{-1}. Anal. Calcd for C$_{46}$H$_{40}$Ni$_1$P$_2$ (713.48): C, 77.44; H, 5.65; Ni, 8.23; P, 8.68. Found: C, 77.42; H, 5.66; Ni, 8.21; P, 8.72.

(PPh$_3$)$_2$Ni(PhC$\equiv$C-*i*-Pr) (4). Method A (yellow microcrystals, 76%): mp 165 °C; ^{1}H NMR δ 0.8 (d, 6 H, 2 CH$_3$, ^{3}J(HH) = 6.7 Hz), 2.22 (m, 1 H, 1 CH), 6.69–6.71 (m, 2 H$_o$, 1 C$_6$H$_5$), 6.97–6.99 (m, 2 H$_m$ and 1 H$_p$, 1 C$_6$H$_5$), 7.07–7.68 (m, 30 H, 2 PPh$_3$); ^{13}C NMR δ 24.11 (d, 2 C, 2 CH$_3$, ^{4}J(PC) = 2.5 Hz), 29.4 (dd, 1 CH, ^{3}J(PC) = 10.45, 3.6 Hz), 126.95 (dd, C^1, ^{2}J(PC) = 36.4, 10.58 Hz), 139.23 (dd, C^2, ^{2}J(PC) = 35.96, 8.1 Hz), 123.64, 127.54–129.32, 132.11–132.74, 134.39–134.81, 135.75, 136.88–138.19 (m, 42 C, 1 C$_6$H$_5$ and 2 PPh$_3$); ^{31}P NMR δ 39.84, 40.99 (^{2}J(PP) = 28.97 Hz); IR ν_{max}(C$\equiv$C) 1815.5 cm^{-1}. Anal. Calcd for C$_{47}$H$_{42}$Ni$_1$P$_2$ (727.51): C, 77.60; H, 5.82; Ni, 8.07; P, 8.51. Found: C, 77.53; H, 5.82; Ni, 8.11; P, 8.61.

(PPh$_3$)$_2$Ni(PhC$\equiv$C-*t*-Bu) (5). Method A (yellow microcrystals, 89%): mp 168 °C; ^{1}H NMR δ 0.78 (s, 9 H, 1 CMe$_3$), 6.57 (m, 2 H$_o$, 1 C$_6$H$_5$), 6.65–6.67 (m, 2 H$_m$ and 1 H$_p$, 1 C$_6$H$_5$), 6.91–7.51 (m, 30 H, 2 PPh$_3$); ^{13}C NMR δ 32.53 (d, 3 C, 3 CH$_3$, ^{4}J(PC) = 1.7 Hz), 33.0 (dd, 1 C, 1 CMe$_3$, ^{3}J(PC) = 7.89, 6.7 Hz), 128.1 (dd, C^1, ^{2}J(PC) = 31.0, 5.5 Hz), 143.15 (dd, C^2, ^{2}J(PC) = 31.0, 5.5 Hz), 123.17, 127.45–129.35, 132.09–132.74, 134.37–136.95, 138.61–139.65 (m, 42 C, 1 C$_6$H$_5$ and 2 PPh$_3$); ^{31}P NMR δ 40.59, 40.75 (^{2}J(PP) = 26.43 Hz); IR ν_{max}(C$\equiv$C) 1785.5 cm^{-1}. Anal. Calcd for C$_{48}$H$_{44}$Ni$_1$P$_2$ (741.53): C, 77.75; H, 5.98; Ni, 7.92; P, 8.35. Found: C, 77.63; H, 5.87; Ni, 7.88; P, 8.25.

(Ph$_3$)$_2$Ni(PhC$\equiv$CH)[22,23] **(6).** Method A (dark brown microcrystals, 53%): mp 89 °C; ^{1}H NMR δ 6.48 (dd, 1 H, ^{3}J(PH) = 26.3, 8.1 Hz), 6.75 (m, 5 H, 1 C$_6$H$_5$), 6.95–7.85 (m, 30 H, 2 PPh$_3$); ^{13}C NMR δ 122.8 (dd, C^1, ^{2}J(PC) = 35.20, 10.06 Hz), 128.48 (dd, C^2, ^{2}J(PC) = 31.2, 8.6 Hz), 124.99, 125.53–130.61, 131.79–132.16, 134.31–135.82, 137.21–137.68 (m, 42 C, 1 C$_6$H$_5$ and 2 PPh$_3$); ^{31}P NMR δ 39.77, 41.06 (^{2}J(PP) = 23.57 Hz); IR ν_{max}(C$\equiv$C) 1752.1 cm^{-1}. Anal. Calcd for C$_{44}$H$_{36}$Ni$_1$P$_2$ (685.43): C, 77.10; H, 5.29; Ni, 8.56; P, 9.04. Found: C, 77.21; H, 5.33; Ni, 8.40; P, 9.10.

(PPh$_3$)$_2$Ni(PhC$\equiv$CSiMe$_3$) (7). Method A (yellow cubes, 88%): mp 125–127 °C dec; ^{1}H NMR δ −0.35 (s, 9 H, 1 SiMe$_3$), 6.65–6.82 (m, 5 H, 1 C$_6$H$_5$), 6.9–7.5 (m, 30 H, 2 PPh$_3$); ^{13}C NMR δ −1.02 (s, 3 C, 1 SiMe$_3$), 128.79 (dd, C^2, ^{2}J(PC) = 30.4, 8.16 Hz), 157.06 (dd, C^1, ^{2}J(PC) = 29.6, 7.7 Hz), 124.15, 127.52–129.38, 132.09–132.73, 134.30–135.37, 136.55–138.81 (m, 42 C, 1 C$_6$H$_5$ and 2 PPh$_3$); ^{31}P NMR δ 38.44, 41.02 (^{2}J(PP) = 30.75 Hz); IR ν_{max}(C$\equiv$C) 1768.0 cm^{-1}. Anal. Calcd for C$_{47}$H$_{44}$Ni$_1$P$_2$Si$_1$ (757.61): C, 74.51; H, 5.85; Ni, 7.75; P, 8.81. Found: C, 74.69; H, 5.97; Ni, 7.72; P, 8.20.

(PPh$_3$)$_2$Ni(PhC$\equiv$CSiPh$_3$) (8). Method A (yellow microcrystals, 52%): mp 134–135 °C dec; ^{1}H NMR δ 6.37–6.57 (m, 5 H, 1 C$_6$H$_5$), 7.92–8.21 (m, 45 H, 1 SiPh$_3$ and 2 PPh$_3$); ^{13}C NMR δ 122.9 (d, C^2, ^{2}J(PC) = 26.74 Hz), 162.3 (d, C^1, ^{2}J(PC) = 22.32 Hz), 123.5, 124.1, 127.11–137.37 (m, 60 C, 1 C$_6$H$_5$, 1 SiPh$_3$ and 2 PPh$_3$); ^{31}P NMR δ 37.69, 39.83 (broad d); IR ν_{max}(C$\equiv$C) 1751 cm^{-1}. Anal. Calcd for C$_{62}$H$_{50}$Ni$_1$P$_2$Si$_1$ (943.82): C, 78.90; H, 5.34; Ni, 6.22; P, 6.56. Found: C, 78.83; H, 5.30; Ni, 6.20; P, 6.53.

(PPh$_3$)$_2$Ni(MeC$\equiv$CSiMe$_3$) (9). Method A (yellow microcrystals, 83%): mp 103 °C; ^{1}H NMR δ −0.29 (s, 9 H, 1 SiMe$_3$), 1.73 (d, 3 H, 1 CH$_3$, ^{4}J(PH) = 5.4 Hz), 7.08–7.72 (m, 30 H, 2 PPh$_3$); ^{13}C NMR δ 1.00 (s, 3 C, 1 SiMe$_3$), 12.53 (dd, 1 C, 1 CH$_3$, ^{3}J(PC) = 12.5, 4.8 Hz), 119.85 (dd, C^2, ^{2}J(PC) = 28.1, 7.7 Hz), 151.75 (dd, C^1, ^{2}J(PC) = 28.7, 9.0 Hz), 127.60–129.38, 132.10–132.75, 133.86–135.73, 137.68–139.05 (m, 36 C, 2 PPh$_3$); ^{31}P NMR δ 38.35, 41.74 (^{2}J(PP) = 34.87 Hz); IR ν_{max}(C$\equiv$C) 1766.4 cm^{-1}. Anal. Calcd for C$_{42}$H$_{42}$Ni$_1$P$_2$Si$_1$ (695.54): C, 72.53; H, 6.09; Ni, 8.44; P, 8.91. Found: C, 72.51; H, 6.11; Ni, 8.44; P, 8.93.

(PCy$_3$)$_2$Ni(PhC$\equiv$CSiMe$_3$) (10). Method B (yellow microcrystals, 67%): mp 138–141 °C dec; ^{1}H NMR δ −0.02 (s, 9 H, 1 SiMe$_3$), 0.86–2.08 (m, 66 H, 6 C$_6$H$_{11}$), 6.90–6.96 (m, 2 H$_m$ and 1 H$_p$, 1 C$_6$H$_5$), 7.06–7.08 (m, 2 H$_o$, 1 C$_6$H$_5$); ^{13}C NMR δ 2.50 (s, 3 C, 1 SiMe$_3$), 14.29, 23.37–37.46 (m, 36 C, 6 C$_6$H$_{11}$), 131.27 (d, C^2, ^{2}J(PC) = 25.83 Hz), 163.50 (d, C^1, ^{2}J(PC) = 24.55 Hz), 123.71, 127.19, 127.67, 145.02 (t, ^{2}J(PC) = 7 Hz, 6 C, 1 C$_6$H$_5$); ^{31}P NMR δ 43.44, 43.61 (^{2}J(PP) = 23.69 Hz); IR ν_{max}(C$\equiv$C) 1699.8 cm^{-1}. Anal. Calcd for C$_{47}$H$_{80}$Ni$_1$P$_2$Si$_1$ (793.89): C, 71.11; H, 10.16; Ni,

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[21] Rosenthal, U.; Oehme, G.; Burlakov, V. V.; Petrovskii, P. V.; Shur, V. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *391*, 119.

[22] Pörschke, R.; Tsay, Yi-Hung; Krüger, C. *Angew. Chem.* **1985**, *97*, 344.

[23] Rosenthal, U.; Schulz, W. *J. Organomet. Chem.* **1987**, *321*, 103.

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotopic Displacement Factors (Å^2 $\times$ 10^{-3})

	x	*y*	*z*	U_{eq}^{a}
Ni	2158 (1)	7465 (1)	3515 (1)	27 (1)*
P(1)	1334 (1)	8408 (1)	4035 (1)	28 (1)*
P(2)	3194 (1)	6364 (1)	3987 (1)	27 (1)*
Si	834 (2)	8932 (2)	2400 (1)	48 (1)*
C(1)	2419 (5)	7319 (5)	2838 (2)	34 (2)*
C(2)	1685 (5)	8036 (5)	2847 (2)	33 (2)*
C(3)	3089 (4)	6677 (4)	2537 (2)	45 (3)*
C(4)	4241	6771	2617	68 (3)*$^+$
C(5)	4880	6136	2342	104 (5)*$^+$
C(6)	4368	5408	1987	130 (7)*$^+$
C(7)	3216	5315	1908	111 (5)*$^+$
C(8)	2577	5949	2183	70 (3)*$^+$
C(9)	1226 (8)	8743 (9)	1774 (3)	131 (5)*
C(10)	−686 (7)	8575 (9)	2333 (3)	116 (5)*
C(11)	916 (12)	10315 (7)	2578 (4)	210 (9)*
C(12)	−177 (3)	8177 (3)	3983 (1)	33 (2)*
C(13)	−677	7600	3564	46 (2)*$^+$
C(14)	−1807	7369	3510	64 (3)*$^+$
C(15)	−2436	7717	3876	58 (3)*$^+$
C(16)	−1936	8294	4296	49 (3)*$^+$
C(17)	−806	8524	4349	41 (2)*$^+$
C(18)	1497 (3)	9843 (3)	3934 (2)	31 (2)*
C(19)	2467	10164	3758	38 (2)*$^+$
C(20)	2692	11245	3710	51 (3)*$^+$
C(21)	1947	12005	3839	55 (3)*$^+$
C(22)	977	11684	4015	67 (3)*$^+$
C(23)	752	10603	4063	47 (3)*$^+$
C(24)	1723 (3)	8324 (2)	4733 (1)	26 (2)*
C(25)	2358	9109	5009	39 (2)*$^+$
C(26)	2669	8993	5531	44 (2)*$^+$
C(27)	2344	8092	5778	39 (2)*$^+$
C(28)	1709	7307	5503	38 (2)*$^+$
C(29)	1398	7423	4980	32 (2)*$^+$
C(30)	4107 (3)	7113 (3)	4468 (1)	28 (2)*
C(31)	4587	8009	4280	38 (2)*$^+$
C(32)	5257	8681	4611	46 (3)*$^+$
C(33)	5448	8457	5129	51 (3)*$^+$
C(34)	4969	7560	5318	48 (2)*$^+$
C(35)	4299	6888	4987	38 (2)*$^+$
C(36)	2484 (3)	5366 (3)	4322 (1)	29 (2)*
C(37)	1329	5345	4233	37 (2)*$^+$
C(38)	751	4613	4490	46 (3)*$^+$
C(39)	1328	3904	4835	49 (3)*$^+$
C(40)	2484	3926	4924	48 (3)*$^+$
C(41)	3061	4657	4667	38 (2)*$^+$
C(42)	4157 (3)	5448 (3)	3736 (1)	33 (2)*
C(43)	5293	5426	3908	45 (3)*$^+$
C(44)	5963	4671	3718	63 (3)*$^+$
C(45)	5497	3938	3355	62 (3)*$^+$
C(46)	4362	3959	3182	56 (3)*$^+$
C(47)	3692	4714	3373	41 (2)*$^+$

[a] Values marked with an asterisk refer to atoms refined with the equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. Values with a plus sign refer to atoms in rigid groups having standard deviations only for the pivot atom.

Table IV. Interatomic Bonding Distances and Bond Angles of Atoms in 7 (with Standard Deviations)

Bond Lengths (Å)			
Ni–P(1)	2.176 (2)	Ni–P(2)	2.151 (2)
Ni–C(2)	1.926 (6)	Ni–C(1)	1.884 (6)
P(1)–C(12)	1.851 (4)	P(1)–C(18)	1.838 (4)
P(1)–C(24)	1.851 (4)	P(2)–C(30)	1.830 (4)
P(2)–C(36)	1.828 (4)	P(2)–C(42)	1.839 (4)
Si–C(2)	1.843 (6)	Si–C(9)	1.814 (8)
Si–C(10)	1.891 (9)	Si–C(11)	1.799 (10)
C(1)–C(2)	1.273 (8)	C(1)–C(3)	1.466 (8)

Bond Angles (deg)			
P(1)–Ni–P(2)	105.4 (1)	P(1)–Ni–C(2)	106.2 (2)
P(2)–Ni–C(2)	148.2 (2)	P(1)–Ni–C(1)	145.0 (2)
P(2)–Ni–C(1)	109.2 (2)	C(2)–Ni–C(1)	39.0 (3)
Ni–P(1)–C(12)	114.5 (1)	Ni–P(1)–C(18)	111.8 (1)
C(12)–P(1)–C(18)	105.8 (2)	Ni–P(1)–C(24)	122.1 (1)
C(12)–P(1)–C(24)	99.9 (2)	C(18)–P(1)–C(24)	100.7 (2)
Ni–P(2)–C(30)	108.9 (1)	Ni–P(2)–C(36)	116.5 (1)
C(30)–P(2)–C(36)	107.2 (2)	Ni–P(2)–C(42)	122.9 (1)
C(30)–P(2)–C(42)	102.7 (2)	C(36)–P(2)–C(42)	97.0 (2)
C(2)–Si–C(9)	108.2 (4)	C(2)–Si–C(10)	111.7 (4)
C(9)–Si–C(10)	105.5 (4)	C(2)–Si–C(11)	114.6 (4)
C(9)–Si–C(11)	110.8 (5)	C(10)–Si–C(11)	105.7 (6)
Ni–C(2)–Si	152.6 (4)	Ni–C(2)–C(1)	68.7 (3)
Si–C(2)–C(1)	138.7 (5)	Ni–C(1)–C(2)	72.3 (4)
Ni–C(1)–C(3)	139.5 (4)	C(2)–C(1)–C(3)	148.2 (5)
C(1)–C(3)–C(4)	120.1 (3)	C(1)–C(3)–C(8)	119.9 (3)
P(1)–C(12)–C(13)	117.1 (1)	P(1)–C(12)–C(17)	122.8 (1)
P(1)–C(18)–C(19)	116.6 (1)	P(1)–C(18)–C(23)	123.2 (1)
P(1)–C(24)–C(25)	121.9 (1)	P(1)–C(24)–C(29)	118.1 (1)
P(2)–C(30)–C(31)	114.1 (1)	P(2)–C(30)–C(35)	125.8 (1)
P(2)–C(36)–C(37)	118.0 (1)	P(2)–C(36)–C(41)	122.0 (1)
P(2)–C(42)–C(43)	123.3 (1)	P(2)–C(42)–C(47)	116.6 (1)

7.39; P, 7.80. Found: C, 71.09; H, 10.09; Ni, 7.36; P, 7.78.

$(P(O\text{-}o\text{-}Tol)_3)_2Ni(PhC{\equiv}CSiMe_3)$ (11). Method B (orange oil, 84%): mp 10 °C; ^{1}H NMR δ 0.17 (s, 9 H, 1 SiMe$_3$), 1.95 (s, 18 H, 6 CH$_3$, 2 P(O-*o*-Tol)$_3$), 6.70–6.99, 7.45–7.49 (m, 29 H, 1 C$_6$H$_5$ and 2 P(O-*o*-Tol)$_3$); ^{13}C NMR δ 0.51 (s, 3 C, 1 SiMe$_3$), 16.75 (s, 6 C, 6 CH$_3$, 2 P(O-*o*-Tol)$_3$), 124.70 (dd, C^2, ^2J(PC) = 35.44, 8.35 Hz), 148.24 (dd, C^1, ^2J(PC) = 39.31, 7.71 Hz), 120.49–120.71, 123.38–126.61, 126.63–128.76, 129.50–129.94, 131.50–131.55, 136.40, 150.83–151.04, 151.05–152.01 (m, 78 C, 1 C$_6$H$_5$ and 2 P(O-*o*-Tol)$_3$); ^{31}P NMR δ 140.94, 141.68 (^2J(PP) = 44.95 Hz); IR ν_{max}(C≡C) 1795 cm^{-1}. Anal. Calcd for $C_{50}H_{56}Ni_1O_6P_2Si_1$ (901.73): Ni, 6.51; P, 6.87. Found: Ni, 6.44; P, 6.78.

$(PCy_3)_2Ni(MeC{\equiv}CSiMe_3)$ (12). Method B (yellow microcrystals, 72%): mp 117 °C dec; ^{1}H NMR δ 0.18 (s, 9 H, 1 SiMe$_3$), 1.26–2.39 (m, 69 H, 1 CH$_3$ and 6 C$_6$H$_{11}$); ^{13}C NMR δ 2.54 (s, 3 C, 1 SiMe$_3$), 15.49 (t, 1 C, 1 CH$_3$, ^2J(PC) = 7.65 Hz), 24.65–37.48 (m, 36 C, 6 C$_6$H$_{11}$), 122.53 (dd, C^2, ^2J(PC) = 34.91, 9.2 Hz), 158.14 (dd, C^1, ^2J(PC) = 36.1, 7.35 Hz); ^{31}P NMR δ 38.35, 41.74 (^2J(PP) = 34.87 Hz); IR ν_{max}(C≡C) 1766.4 cm^{-1}. Anal. Calcd for $C_{42}H_{78}Ni_1P_2Si_1$ (731.82): C, 68.93; H, 10.74; Ni, 8.02; P, 8.46. Found: C, 68.91; H, 10.71; Ni, 8.06; P, 8.48.

$(P(O\text{-}o\text{-}Tol)_3)_2Ni(MeC{\equiv}CSiMe_3)$ (13). Method B (orange oil, 70%): mp −20 °C; ^{1}H NMR δ −0.02 (s, 9 H, 1 SiMe$_3$), 2.05 (s, 3 H, 1 CH$_3$), 2.19 (s, 18 H, 2 P(O-*o*-Tol)$_3$), 6.86–7.36 (m, 24 H, 2 P(O-*o*-Tol)$_3$); ^{13}C NMR δ 1.80 (s, 3 C, 1 SiMe$_3$), 16.18 (s, 6 C, 6 CH$_3$, 2 P(O-*o*-Tol)$_3$), 16.60 (s, 1 C, 1 Me), 124.63 (dd, C^2, ^2J(PC) = 34.92, 8.05 Hz), 148.23 (dd, C^1, ^2J(PC) = 38.7, 7.2 Hz), 119.6, 120.33–121.16, 123.61–124.83, 126.02–127.68, 129.74–130.40, 131.14–132.45, 136.3, 149.8, 151.0 (m, 36 C, 6 C$_6$H$_4$, 2 P(O-*o*-Tol)$_3$); ^{31}P NMR δ 141.33, 141.70 (^2J(PP) = 57.0 Hz); IR ν_{max}(C≡C) 1816.0 cm^{-1}. Anal. Calcd for $C_{45}H_{54}Ni_1O_6P_2Si_1$ (839.66): Ni, 6.99; P, 7.38. Found: Ni, 6.94; P, 7.32.

X-ray Crystal Structure Determination of 7: approximate crystal size 0.22 × 0.18 × 0.12 mm^3; Nicolet R3m/V diffractometer; Mo Kα radiation (graphite monochromator); T = 220 K; cell dimensions a = 12.200 (2) Å, b = 12.564 (2) Å, c = 26.607 (4) Å, α = 90°, β = 98.37 (1)°, γ = 90°, V = 4034.8 (1.1) Å^3, Z = 4, d_{calcd} = 1.247 g/cm^3, μ = 0.62 mm^{-1}; monoclinic; space group $P2_1/c$; data collection ($2\theta_{max}$ = 45°) of 5327 independent intensities, 3397 of which treated as observed ($F_o = 4\sigma(F)$). Structure solution was by Patterson method and full-matrix least-squares refinement was done using SHELXTL-PLUS; phenyl rings and hydrogen atoms were treated as rigid groups, and hydrogen atoms were given isotropic displacement parameters for each group. A total of 386 parameters were refined, R = 0.052, R_w = 0.048, $w^{-1} = \sigma^2(F) + 0.00038F^2$, with a maximum residual electron density (1.22 Å from H(11)) of 0.5 e/Å^3.

Results and Discussion

The model of transition-metal–olefin bonding suggested by Dewar, Chatt, Duncanson, and Nelson et al. can also be applied for the interpretation of the metal–acetylene bond.[24,25] In accordance with this, Stone supposed in his

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(24) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79.

(25) (a) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, *2939*. (b) Nelson, J. H.; Wheelock, K. S.; Cusachs, L. C.; Jonassen, H. B. *J. Am. Chem. Soc.* **1969**, *91*, 7005.

Table V. H Atom Coordinates ($\times 10^4$) and Isotropic Atomic Displacement Factors ($Å^2 \times 10^{-3}$)

	x	y	z	U^a
H(4)	4594	7272	2861	194 (20)
H(5)	5673	6201	2396	194 (20)
H(6)	4808	4972	1798	194 (20)
H(7)	2863	4814	1664	194 (20)
H(8)	1784	5885	2128	194 (20)
H(9A)	1994	8917	1782	162 (25)
H(9B)	1105	8013	1676	162 (25)
H(9C)	781	9194	1534	162 (25)
H(10A)	−1012	9151	1998	320 (48)
H(10B)	−875	8423	2711	320 (48)
H(10C)	−817	7616	2306	320 (48)
H(11A)	1675	10543	2619	180 (28)
H(11B)	490	10730	2316	180 (28)
H(11C)	627	10410	2892	180 (28)
H(13)	−244	7361	3312	69 (9)
H(14)	−2151	6972	3222	69 (9)
H(15)	−3214	7558	3840	69 (9)
H(16)	−2369	8533	4548	69 (9)
H(17)	−462	8921	4638	69 (9)
H(19)	2980	9641	3669	106 (12)
H(20)	3359	11466	3588	106 (12)
H(21)	2102	12749	3805	106 (12)
H(22)	464	12207	4104	106 (12)
H(23)	85	10382	4185	106 (12)
H(25)	2581	9729	4839	70 (9)
H(26)	3106	9533	5721	70 (9)
H(27)	2558	8012	6138	70 (9)
H(28)	1486	6687	5673	70 (9)
H(29)	961	6883	4790	70 (9)
H(31)	4455	8164	3923	60 (9)
H(32)	5587	9298	4481	60 (9)
H(33)	5910	8919	5357	60 (9)
H(34)	5101	7406	5675	60 (9)
H(35)	3969	6272	5117	60 (9)
H(37)	931	5833	3995	54 (8)
H(38)	−44	4599	4429	54 (8)
H(39)	931	3401	5011	54 (8)
H(40)	2881	3438	5161	54 (8)
H(41)	3856	4672	4728	54 (8)
H(43)	5613	5931	4158	70 (10)
H(44)	6745	4656	3837	70 (10)
H(45)	5959	3418	3224	70 (10)
H(46)	4041	3454	2932	70 (10)
H(47)	2910	4729	3254	70 (10)

^{a} Atoms in rigid groups without standard deviations.

earlier work a "metallacycle type" structure to explain the interaction of platinum and substituted acetylene ligands.[26] Accepting this proposal, we hoped to get more information and better insight into the electron distribution of the quasi-aromatic carbon–nickel π-system using spectroscopic methods: especially measuring the electron density of quaternary carbon atoms using ^{13}C NMR spectroscopy.

Valuable information can be obtained by measuring the influence of electron donor and acceptor ring substituents on the electron distribution of the metallacycle. In order to determine this influence, a series of nonsymmetrically substituted acetylenes have been synthesized. To evaluate the data, the symmetrical acetylene tolan was used as standard and one of the phenyl groups was systematically replaced by various substituents. Figure 2 shows how the polarization of the bond between two quaternary carbon atoms (in the case of two nonsymmetrical acetylenes) changes depending on the substituents, as compared to the symmetrically substituted acetylene used as reference. As it can be concluded, the influence of substituents is stronger on the quaternary carbon atom in the position β to the appropriate substituent.

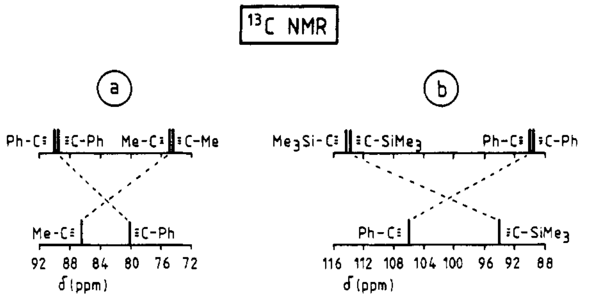

Figure 2. Development of bond polarization between the two sp carbon atoms of nonsymmetrically substituted acetylenes: (a) σ-donor substituent (Me and Ph); (b) σ-donor and π-acceptor substituent ($SiMe_3$ and Ph). Quaternary C atoms of symmetrically substituted acetylenes give only one NMR signal. The bold (doubled) line refers to the degeneration of the electronic state of the two C atoms. When they are perturbated by nonequal substitution, degeneration ceases and two signals can be observed.

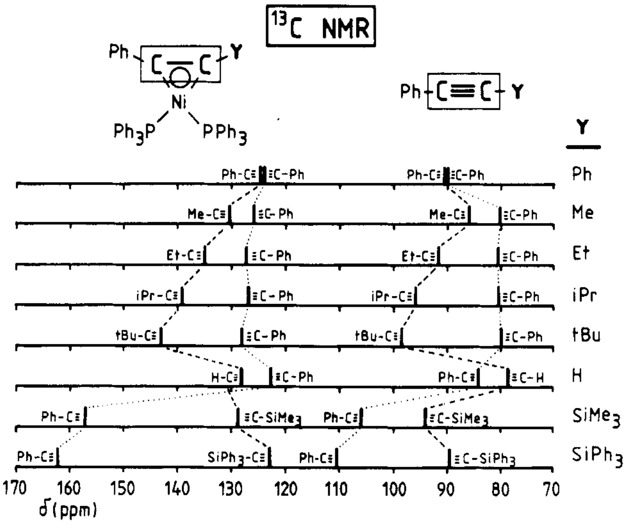

Figure 3. ^{13}C NMR chemical shifts of the appropriate carbon atoms of free and nickel-coordinated acetylenes.

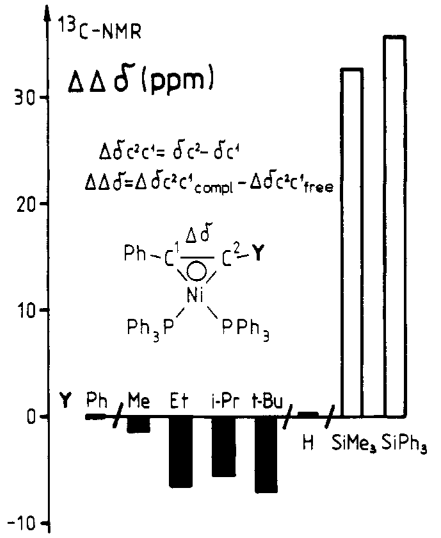

Figure 4. Decreased (−ΔΔδ) and increased (+ΔΔδ) polarization of the triple bond concerning the free acetylene dependent on the substituent Y in complexes of the type $(PPh_3)_2Ni(PhC^1{\equiv}C^2Y)$.

Figure 3 shows the comparison of the nonsymmetrical acetylene substitution. The effect on the quaternary carbon atoms can be followed well both for the free acetylenes and the metallacycles formed. It should be concluded that the characteristic chemical shift differences

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[26] Boag, N. M.; Green, M.; Grove, D. M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 2170.

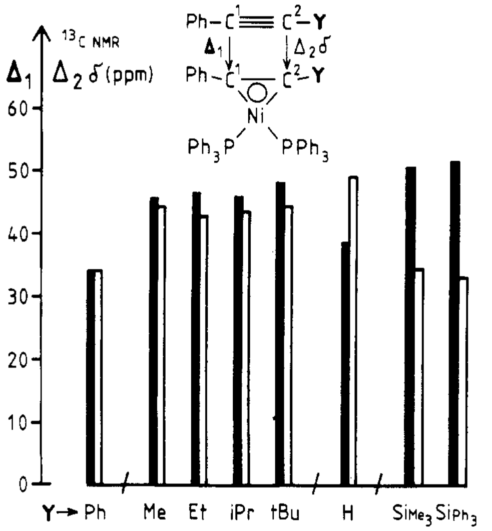

Figure 5. Change of $\Delta\delta = \delta_{coord} - \delta_{free}$ values for quaternary carbon atoms of $(PPh_3)_2Ni(PhC^1{\equiv}C^2Y)$ type complexes depending on the Y substituent.

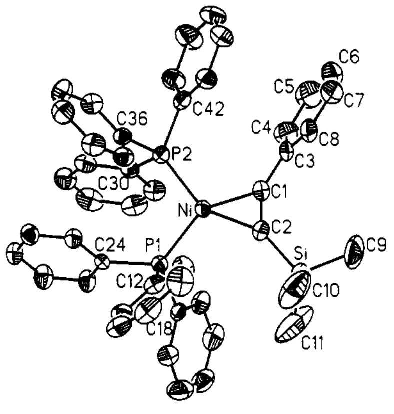

Figure 6. Structure of $(PPh_3)_2Ni(PhC^1{\equiv}C^2SiMe_3)$.

of quaternary carbon atoms of nonsymmetrical free acetylenes in the case of alkyl substituents are decreased while in cases of trimethylsilyl and triphenylsilyl substituents they are further increased by coordination to the $(PPh_3)_2Ni$ fragment. These tendencies are presented in Figure 4.

The results also show how the electron densities of the two acetylene carbon atoms C^1 and C^2 are altered separately due to complexation to the transition metal. This effect is characterized by the complexation shift Δδ (^{13}C NMR: $\Delta\delta = \delta_{coord} - \delta_{free}$). In the case of symmetrically substituted acetylenes such as tolan, the values of Δδ are the same for both acetylene carbon atoms. However, with replacement one of the phenyls with alkyl substituents the change of the electron density of the two quaternary carbon atoms is significantly different. The complexation shifts ($\Delta_1\delta$ for C^1 and $\Delta_2\delta$ for C^2) of both acetylene C atoms depending on the substituents are presented in Figure 5.

From our experiments (Figures 3–5) it became evident that systematically applied α-methyl perturbation at the sp^3 carbon atom in the form of alkyl group variation (CH_3, CH_2Me, $CHMe_2$, CMe_3)[27,28] caused in the metallacycles a decrease in polarization of the bond between the C^1 and C^2 atoms relative to free acetylenes and led to a mild alternating interaction between C^1, C^2, and the $(PPh_3)_2Ni$ fragment (see the differences of $\Delta_1\delta$ and $\Delta_2\delta$ in Figure 5). A stronger effect can be observed for H and for substituents connected by a heteroatom to the acetylene base fragment, as exemplified by the cases of Y = $SiMe_3$ and $SiPh_3$.

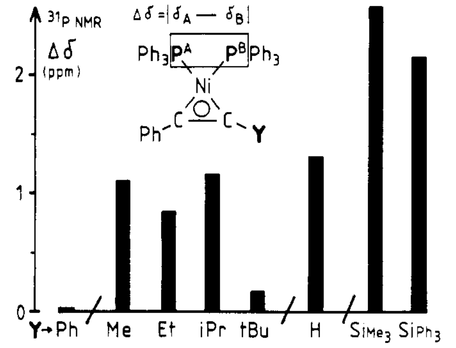

Figure 7. Chemical shift difference of phosphorus atoms (AB/AX system) for $(PPh_3)_2Ni(PhC{\equiv}CY)$ type complexes with various Y substituents.

It can also be stated that all acetylenes with the exception of phenylacetylene show a reverse of polarization of the bond between the quaternary carbon atoms on complexation. It is very important to emphasize that H is the only substituent that has exclusively a spherical (s) orbital symmetry character. Not only does this type of s/p electronic property change in symmetry lead to very definite effects in organometallic chemistry, but also this information-bearing perturbation can be recognized in the structure of naturally occurring amino acids selected by evolution (see ref 28, p 168).

Our spectroscopic measurements (^{13}C NMR analysis) prove that the silyl substituents cause the largest polarization of the bond between acetylene carbon atoms in these metallacycles. This means that in these complexes the C^1 and C^2 quaternary carbon atoms must have a significantly different degree of interaction with the central nickel atom. This statement is supported by the X-ray structure determination of the $(PPh_3)_2Ni(PhC^1{\equiv}C^2SiMe_3)$ complex which shows significantly different C^1—Ni and C^2—Ni distances. The structure has an essentially trigonal-planar coordination geometry around the Ni atom, if the coordinated triple bond of the acetylene is assumed to occupy one coordination site. The planarity of the inner coordination sphere is indicated by a small dihedral angle of about 3.2° between the NiC^{1}C^2 and NiP^{1}P^2 planes. The angles P^{1}NiP^2 and C^{1}NiC^2 are 105.4 (1) and 39.0 (3)°, respectively. The acetylene ligand adopts a cis-bent configuration, with a mean deviation from linearity of 41.3 (5)° (C^{1}C^{2}Si) and 31.8 (5)° (C^{3}C^{1}C^2). These angles have generally a value of about 40°. Similar bend-back angles of 38.2 (2) and 41.0 (2)° have also been found in the case of the nonsymmetrically substituted platinum complex $(PPh_3)_2Pt(PhC{\equiv}CMe)$.[29] In this latter case, since there is no silyl group in the molecule, the difference between the angles is significantly smaller than in complex **7**. The coordinated triple-bond length in complex **7** is 1.273 (8) Å.

The $L_2Ni(PhC{\equiv}CY)$ type complexes were studied also by ^{31}P NMR spectroscopy, to determine the influence of the acetylene substituents on the phosphorus atoms. Figure 7 shows again an alternation using the alkyl variation Me, Et, *i*-Pr, and *t*-Bu. The biggest differences can be observed in the case of silyl-substituted acetylenes and the smallest one for the *t*-Bu substituent.

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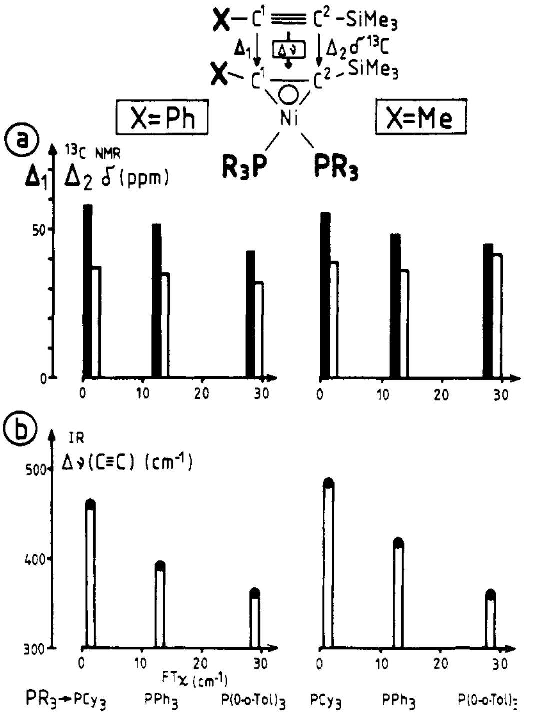

Figure 8. (a) Electron density ($\delta^{13}C$) of the three-membered ring carbon atoms depending on the electronic parameters ($^{FT}\chi$) of tertiary phosphines. (b) Degree of strength of complexation characterized by the ν(C≡C) values.

This is an additional interesting example for the various effects due to the presence of *t*-Bu and $SiMe_3$ groups. They are very similar in their steric and σ_I parameters.[30] Consequently, the difference in their effects in our molecules can only be explained by supposing the existence of $d\pi$–$p\pi$ interaction ($SiMe_3$) or nonexistence of it (*t*-Bu). Thus far we have discussed the effect of substituents on the behavior of the metallacycle. However, in these complexes the phosphine ligands can also have an influence on the already polarized metallacycle. This effect is investigated using two strongly polarized acetylenes containing trimethylsilyl substituents (X = Ph, Me; Y = $SiMe_3$) and various phosphine ligands.

Figure 8a shows the change of electron density of the three-membered ring carbon atoms (as compared to the free acetylenes) depending on the electronic parameters ($^{FT}\chi^{31}$) of the tertiary phosphines used. In fact, a surprisingly significant effect can be observed. With the strong donor ligand PCy_3, the polarization of the bond between the acetylene carbon atoms increases further relative to the free acetylene triple bond while that of the strong acceptor type ligand P(O-*o*-Tol)$_3$ seems to get lower with the difference in the electron densities.

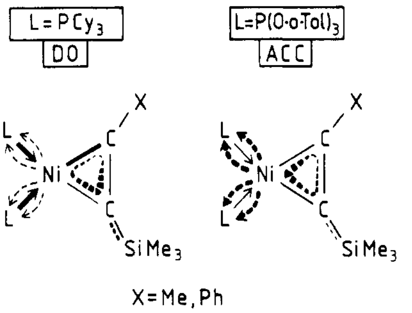

Figure 9. Effect of donor and acceptor type phosphorus ligands on the electron distribution conditions of the metallacycle.

Figure 8b shows the $\Delta\nu$(C≡C) values which are regarded to be characteristic for the degree of strength of complexation.[32] It can be seen that as a tendency the strength of acetylene coordination decreases with the increase of the acceptor character of the ligand. The qualitative electron distributions in the metallacycle having the above mentioned phosphorus ligands are summarized in Figure 9. It should be noted that electron distributions based on our measurements refer only to electron densities (amplitude information); however, they provide no data on the orbital symmetries (phase information).

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Supplementary Material Available: Listings of crystal structure data and anisotropic displacement factors (4 pages); a table of structure factors (19 pages). Ordering information is given on any current masthead page.

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