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COORDINATION COMPLEXES OF ACETYLENIC PHOSPHINES AND DIPHOSPHINES

VI. CARBONYL-AND π-CYCLOPENTADIENYL-NICKEL DERIVATIVES OF 3,3,3-TRIMETHYLPROPYNYLDIPHENYLPHOSPHINE AND PHENYLETHYNYLDIPHENYLPHOSPHINE

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Summary

The reactions of π-cyclopentadienylnickel carbonyl dimer with 3,3,3-trimethylpropynyldiphenylphosphine and phenylethynyldiphenylphosphine are described. The products have been characterized by elemental and mass spectral analysis, infrared and NMR spectroscopy. An acetylene bridged complex $(\pi\text{-}C_5H_5Ni)_2Ph_2PC_2\text{-t-Bu}$, containing an uncoordinated phosphorus atom, has been prepared. The complex can be oxidized to the phosphine oxide derivative $(\pi\text{-}C_5H_5Ni)_2Ph_2P(O)C_2\text{-t-Bu}$ and converted to the phosphonium salts $(\pi\text{-}C_5H_5Ni)_2(Ph_2P(R)C_2\text{-t-Bu})X$ ($R = Me$, $X = I$; $R = Et$, $X = Br$) via reaction with methyl iodide or ethyl bromide. These are the first reported π-complexes of phosphonium salts. The complex $(\pi\text{-}C_5H_5Ni)_2Ph_2PC_2\text{-t-Bu}$ forms the novel mixed metal derivative $[PdCl_2][(\pi\text{-}C_5H_5Ni)_2Ph_2PC_2\text{-t-Bu}]_2$ from bis(benzonitrile)-palladium dichloride. The dicarbonyl complexes $Ni(CO)_2(Ph_2PC_2R)_2$ ($R = \text{t-Bu}$, Ph), the phosphine oxide complex $(\pi\text{-}C_5H_5Ni)_2(Ph_2P(O)C_2Ph)$ and the trinuclear nickel carbonyl derivative $Ni(CO)_3[(\pi\text{-}C_5H_5Ni)_2Ph_2PC_2Ph]$ are described.

Introduction

The phosphinoacetylenes $R_2PC{\equiv}CR'$ are potentially ambidentate ligands with a capacity to coordinate as simple phosphines [1], as disubstituted acetylenes [2] or to utilize simultaneously the phosphorus lone pair and acetylenic π-orbitals in a polydentate bonding mode [3, 4]. Although all three of these possibilities have been realized it is apparent that phosphine behavior predominates for complexes of metals in their normal oxidation states while participation of the acetylenic triple bond in coordination requires a low valent metal site with a high affinity for alkyne π-electrons [2—4]. Furthermore, even in the latter situation, the phosphorus atom may compete effectively for the available site, as evidenced by the failure to prepare π-acetylene complexes of palladium(0) and platinum(0) from $(Ph_3P)_4M$ (M = Pd, Pt) and $Ph_2PC{\equiv}CPPh_2$ or from $MCl_2(Ph_2PC{\equiv}CMe)_2$ (M = Pd, Pt) by hydrazine reduction in the presence of excess ligand [5]. The present work was motivated by a search for simple phosphinoacetylene π-complexes for studies of acetylene oligomerisation reactions. In addition, a report that only one product, $Ni(CO)(Ph_2PC{\equiv}CPh)_3$, was characterized from the reaction of $[\pi\text{-}C_5H_5Ni(CO)]_2$ with $Ph_2PC{\equiv}CPh$ [6] seemed at variance with recent work describing the synthesis and structures of a range of phosphinoacetylene bridged tetracobalt decacarbonyl complexes [2]. The well-established structural analogy between the alkyne bridged $Co_2(CO)_6(RC{\equiv}CR)$ [7] and $(\pi\text{-}C_5H_5Ni)_2(RC{\equiv}CR)$ [8] complexes suggested that compounds related to the latter should be readily available from $[\pi\text{-}C_5H_5Ni(CO)]_2$ or $(\pi\text{-}C_5H_5)_2Ni$ and $Ph_2PC{\equiv}CR$. This paper describes in detail the reactions of $[\pi\text{-}C_5H_5Ni(CO)]_2$ and $(\pi\text{-}C_5H_5)_2Ni$ with $Ph_2PC{\equiv}CR$ (R = Ph, t-Bu).

The alkyne bridged complex $(\pi\text{-}C_5H_5Ni)_2Ph_2PC_2\text{-t-Bu}$ contains an uncoordinated phosphorus atom which can be oxidized, quaternized or utilized as a σ-donor in forming the novel mixed metal complex $PdCl_2[(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2\text{-t-Bu})]_2$. The dicarbonyl complexes $Ni(CO)_2(Ph_2PC{\equiv}CR)_2$ (R = Ph, t-Bu) and the trinuclear carbonyl complex $Ni(CO)_3[(\pi\text{-}C_5H_5Ni)_2Ph_2PC_2Ph]$ are also described.

Experimental

Nickelocene $(\pi\text{-}C_5H_5)_2Ni$ was purchased from Research Organic Inorganic Chemical Corporation, Sun Valley, California. π-Cyclopentadienylnickel carbony dimer, $[\pi\text{-}C_5H_5Ni(CO)]_2$ was prepared by the method of Tilney—Bassett [9]. The phosphinoacetylenes $Ph_2PC{\equiv}C\text{-t-Bu}$ and $Ph_2PC{\equiv}CPh$ were synthesized as previously described [10]. The solvents benzene, petroleum ether, diethyl ether and cyclohexane were dried and deoxygenated by refluxing over lithium aluminum hydride under a nitrogen atmosphere. A nitrogen atmosphere was routinely employed for carrying out reactions, chromatography, subsequent work-up an recrystallization. Chromatographic alumina and silica gel were Fisher A-540 and Merck Type 60 (30-70 mesh ASTM) respectively.

Microanalyses were carried out by Galbraith Laboratories. Perkin—Elmer 180 and 457 spectrophotometers were used for infrared measurements. Nuclear magnetic resonance spectra were recorded on a Varian T-60 spectrometer and mass spectra on an AEI MS 30 instrument at 70 eV.

Reaction of $(\pi\text{-}C_5H_5)_2Ni$ *with* $Ph_2PC{\equiv}C\text{-t-Bu}$

A mixture of $(\pi\text{-}C_5H_5)_2Ni$ (0.1 g; 5.3 mmol) and $Ph_2PC{\equiv}C\text{-t-Bu}$ (1.33 g; 5.0 mmol) in benzene (50 ml) was refluxed for 12 h. The green solution was cooled, filtered under nitrogen and the solvent reduced to small volume. Careful chromatography on a silica-gel column made up in petroleum ether (80—100°) eluted the bands listed in Table 1. During chromatography some of the free ligand $Ph_2PC{\equiv}C\text{-t-Bu}$ was oxidized on the column to $Ph_2P(O)C{\equiv}C\text{-t-Bu}$. Removal of solvent from the green solution obtained from the third band followed by addition of a few mls of petroleum ether and cooling at 0° gave green crystals of $(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2\text{-t-Bu})$ (5%). This compound is very air sensitive in solution

TABLE 1

Band	Color	Eluant	Compound
1	Blue-green	Petr.-ether	$(\pi\text{-}C_5H_5)_2Ni$
2	Pale-yellow	Petr.-ether	$Ph_2PC{\equiv}C\text{-t-Bu}$
3	Green	Benzene	$(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2\text{-t-Bu})$
4	Green	Ether/acetone	$(\pi\text{-}C_5H_5Ni)_2(Ph_2P(O)C_2\text{-t-Bu})$

and slowly decomposes in air. (Found: C, 65.20; H, 5.68; P, 5.83; Ni, 22.72. Calcd.: C, 65.43; H, 5.69; P, 6.03; Ni, 22.85%.)

The solution from band four was taken to dryness and the residue recrystallized from benzene/petroleum ether to yield green crystals of $(\pi\text{-}C_5H_5Ni)_2\text{-}(Ph_2P(O)C_2\text{-t-Bu})$ (Found: C, 63.49; H, 6.05. Calcd.: C, 63.47; H, 5.48%.)

Reaction of $[\pi\text{-}C_5H_5Ni(CO)]_2$ *with* $Ph_2PC_2\text{-t-Bu}$

A solution containing $[\pi\text{-}C_5H_5Ni(CO)]_2$ (0.92 g; 3.0 mmol) and $Ph_2PC{\equiv}C\text{-t-Bu}$ (1.33 g; 5.0 mmol) in benzene (50 ml) was refluxed under nitrogen for 24 h during which time the color changed from the bright red of $[\pi\text{-}C_5H_5Ni(CO)]_2$ to yellowish-brown and finally green. The green solution was cooled, filtered and chromatographed giving the bands described in Table 2.

Pale-yellow crystals of the dicarbonyl complex were obtained from the residue of band 1 on recrystallization from petroleum ether (10%). (Found: C, 69.73; H, 5.86. Calcd.: C, 70.50; H, 5.92%.)

The compound obtained from band 3 was present in only minute quantities and characterization was not attempted. The remaining two compounds proved to be identical to those obtained from the reaction with nickelocene.

TABLE 2

Band	Color	Eluant	Compound
1	Pale-yellow	Petr.-ether	$Ni(CO)_2(Ph_2PC{\equiv}C\text{-t-Bu})_2$
2	Blue-green	Petr.-ether	$(\pi\text{-}C_5H_5)_2Ni$
3	Yellow-brown	Petr.-ether	
4	Green	Benzene	$(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2\text{-t-Bu})$
5	Green	Ether/acetone	$(\pi\text{-}C_5H_5Ni)_2(Ph_2P(O)C_2\text{-t-Bu})$

Reaction of $[\pi\text{-}C_5H_5Ni(CO)]_2$ *with* $Ph_2PC{\equiv}CPh$

A mixture of $[\pi\text{-}C_5H_5Ni(CO)]_2$ (1.6 g; 5.3 mmol), $Ph_2PC{\equiv}CPh$ (1.70 g; 5.9 mmol) and cyclohexane (6 ml) was sealed in a Carius tube and heated in an oven at 60° overnight. The red color gradually changed to greenish-brown and a dark solid precipitated. The sealed tube was opened under nitrogen, solvent removed and the residue dissolved in a minimum of benzene. Chromatography on an alumina column made up in petroleum ether yielded the bands mentioned in Table 3. Recrystallization of the solid from band 2 in ethanol gave pale yellow crystals of $Ni(CO)_2(Ph_2PC{\equiv}CPh)_2$ (12%). (Found: C, 73.02; H, 4.51; P, 8.90. Calcd.: C, 73.39; H, 4.37; P. 9.03%.) The same compound was prepared by refluxing 2 moles of $Ph_2PC{\equiv}CPh$ with $Ni(CO)_4$ in ethanol for 6 h followed by recrystallization from the same solvent.

TABLE 3

Band	Color	Eluant	Compound
1	Pale-yellow	Petr.-ether	$(\pi\text{-}C_5H_5)_2Ni$
2	Yellow	Petr.-ether	$Ni(CO)_2(Ph_2PC{\equiv}CPh)_2$
3	Pale-yellow	Petr.-ether	$Ph_2PC{\equiv}CPh$
4	Green	4/1 Petr.-ether/benzene	$Ni(CO)_3[(\pi\text{-}C_5H_5Ni)_2Ph_2PC_2Ph]$
5	Green	4/1 Petr.-ether/benzene	Not characterized
6	Green	1/1 Benzene/ether	$(\pi\text{-}C_5H_5Ni)_2(Ph_2P(O)C{\equiv}CPh)$

The solution from band 4 was reduced in volume, degassed heptane added and the solution filtered with a filter stick. The filtrate yielded green crystals of $Ni(CO)_3[(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2Ph)]$ on cooling (23%). (Found: C, 58.84; H, 3.75; P, 4.45. Calcd.: C, 58.58; H, 3.72; P, 4.53%.)

Green crystals of the oxide complex $(\pi\text{-}C_5H_5Ni)_2(Ph_2P(O)C_2Ph)$ were obtained on recrystallization of the solid residue from band 6 in cyclohexane. (Found: C, 65.98; H, 4.53; P, 5.70. Calcd.: C, 65.70; H, 4.66; P, 5.74%.)

Reaction of $[\pi\text{-}C_5H_5Ni(CO)]_2$ with $Ph_2PC{\equiv}CPh$ at 60° for 72 h

These reaction conditions were those used by Efraty and King [6]. In agreement with these workers the major product under these conditions is $Ni(CO)(Ph_2PC{\equiv}CPh)_3$.

Reaction of $(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2\text{-t-Bu})$ with CH_3I and C_2H_5Br

A sample of $(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2\text{-t-Bu})$ (250 mg) dissolved in dry benzene was stirred with a slight excess of CH_3I for 24 h. Dark green crystals of $(\pi\text{-}C_5H_5Ni)\cdot(Ph_2P(Me)C_2\text{-t-Bu})I$ were formed (62%). (Found: C, 53.30; H, 5.24. Calcd.: C, 53.11; H, 4.88%).

An analogous reaction with C_2H_5Br yielded dark green crystals of $(\pi\text{-}C_5H_5Ni)_2(Ph_2P(C_2H_5)C_2\text{-t-Bu})Br$ (51%). (Found: C, 57.85; H, 5.50. Calcd.: C, 57.81; H, 5.57%.)

Reaction of $(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2\text{-t-Bu})$ with trans-$(PhCN)_2PdCl_2$

Reaction of $(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2\text{-t-Bu})$ (50 mg; 0.1 mmol) in dry benzene for 18 h with the stoichiometric quantity of *trans*-$(PhCN)_2PdCl_2$ gave dark brown microcrystals of the complex $PdCl_2[(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2\text{-t-Bu})]_2$ which crystallized with half a mole of benzene (65%) (Found: C, 57.02; H, 5.38; P, 4.63; Cl, 6.47. Calcd.: C, 56.95; H, 4.94; P, 4.97; Cl, 5.71%.)

Reaction of $Ni(CO)_4$ with $Ph_2PC{\equiv}C\text{-t-Bu}$

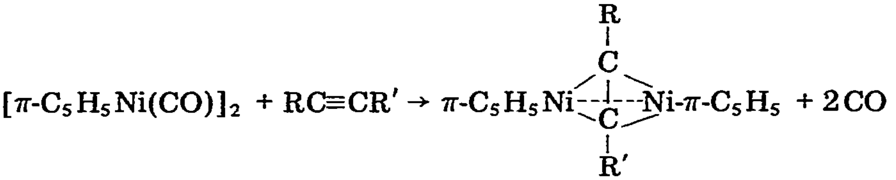
On treating $Ni(CO)_4$ (0.42 g; 2.5 mmol) with $Ph_2PC{\equiv}C\text{-t-Bu}$ (1.33 g; 5 mmol) in dry ethanol (or ether) at reflux for several minutes a yellow precipitate was obtained. This was filtered off and the filtrate cooled to yield pale yellow crystals of $Ni(CO)_2(Ph_2PC{\equiv}C\text{-t-Bu})_2$, characterized above.

Results and discussion

Cyclopentadienylnickel carbonyl dimer generally reacts with phosphines according to eqn. 1 [11, 12], although there are two known instances in which

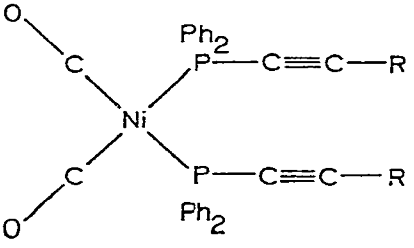
$$[\pi\text{-}C_5H_5Ni(CO)]_2 + 2L \rightarrow Ni(CO)_2L_2 + (\pi\text{-}C_5H_5)_2Ni \qquad (1)$$

the major phosphine containing product is a monocarbonyl tris(phosphine) complex [6, 13]. Acetylenes displace the bridging carbon monoxide ligands of $[\pi\text{-}C_5H_5Ni(CO)]_2$, affording alkyne bridged complexes (eqn. 2) [9, 14]. The latter reaction is however complicated by decomposition of $[\pi\text{-}C_5H_5Ni(CO)]_2$



$$[\pi\text{-}C_5H_5Ni(CO)]_2 + RC{\equiv}CR' \rightarrow \pi\text{-}C_5H_5Ni\overset{\overset{R}{|}}{\underset{\underset{R'}{|}}{C{-}C}}Ni\text{-}\pi\text{-}C_5H_5 + 2CO \qquad (2)$$

to the trimer $(\pi\text{-}C_5H_5)_3Ni_3(CO)_2$, nickelocene and nickel carbonyl [15]. The same alkyne bridged complexes are accessible from the reaction of nickelocene with acetylenes [14, 16]. The phosphinoacetylenes $Ph_2PC{\equiv}CR$ (R = t-Bu, Ph) show behavior characteristic of both phosphines and disubstituted alkynes in their reactions with $[\pi\text{-}C_5H_5Ni(CO)]_2$. Three new complexes were isolated by chromatography in each case. The pale yellow complex $Ni(CO)_2(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ was characterized as a disubstituted phosphine derivative (I) of $NI(CO)_4$



(I)

on the basis of microanalysis, a mass spectrum (Table 4) exhibiting a parent ion peak at *m/e* 646 and ions at *m/e* 618, 590 due to consecutive loss of two carbonyl groups and infrared spectra in the ν(CO) region (Table 5) typical of other $Ni(CO)_2L_2$ (L = tertiary phosphine) species [cf. $Ni(CO)_2(Ph_3P)_2$; ν(CO) C_6H_{12}; 2010, 1955 cm^{-1} [17]. The presence of two $\nu(C{\equiv}C)$ bands at 2201, 2160 cm^{-1} close to those of the free ligand [10] ruled out participation of the C≡C-bonds in coordination. Characterization was completed by an independent synthesis from $Ni(CO)_4$. Similar arguments apply to the compound $Ni(CO)_2(Ph_2PC{\equiv}CPh)_2$ obtained from $[\pi\text{-}C_5H_5Ni(CO)]_2$ or $Ni(CO)_4$ and $Ph_2PC{\equiv}CPh$ which therefore has a structure analogous to I. We have confirmed that the major product obtained on treating $Ni(CO)_4$ with $Ph_2PC{\equiv}CPh$ in refluxing benzene for 3 days is the monocarbonyl derivative $Ni(CO)(Ph_2PC{\equiv}CPh)_3$ as previously reported [6].

The green air-sensitive complex $(\pi\text{-}C_5H_5Ni)_2(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)$ shows a parent ion at *m/e* 512 in the mass spectrum (Table 4). This ion fragments by loss of a PPh_2 radical, a neutral C_5H_6 molecule, a neutral tert-butylacetylene mole-

TABLE 4

MASS SPECTRA AT 70 eV OF NICKEL COMPLEXES [a]

Compound	*m/e* (Relative abundance)					
$(\pi\text{-}C_5H_5Ni)_2Ph_2\text{-}PC_2\text{-}t\text{-}Bu$	512(15)	446(8)	430(2)	390(2)	370(2)	364(1)
	354(1)	327(9)	312(1)	308(1)	282(4)	266(100)
	262(33)	251(19)	246(5)	210(22)	188(39)	183(47)
	180(53)	178(39)	158(72)	154(54)	143(250)	128(139)
	123(24)	115(308)	91(84)	77(85)		
$(\pi\text{-}C_5H_5Ni)_2Ph_2\text{-}P(O)C_2\text{-}t\text{-}Bu$	528(79)	463(8)	447(6)	405(36)	340(28)	
	324(11)	305(11)	281(93)	266(58)	259(44)	
	245(24)	201(36)	188(100)	158(30)	143(86)	
	128(41)	123(57)	115(20)	91(35)	81(28)	
	77(50)					
$Ni(CO)_2\text{-}(Ph_2PC_2\text{-}t\text{-}Bu)_2$	648(6)	618(1)	590(1)	490(2)	428(1)	423(3) 413(10
	397(1)	385(2)	383(2)	373(4)	369(1)	324(4)
	300(7)	282(100)	266(170)	251(12)	237(57)	221(99)
	209(260)	189(110)				
$(\pi\text{-}C_5H_5Ni)_2Ph_2\text{-}P(O)C_2Ph$	548(41)	450(10)		424(23)	404(1)	
	360(40)	347(4)	324(3)	312(4)	307(5)	
	306(5)	305(11)	302(9)	301(17)	283(4)	
	282(3)	260(4)	258(5)	250(5)	249(13)	
	248(19)	238(7)	236(15)	225(14)	219(25)	
	201(10)	190(10)	188(26)	179(20)	178(100)	
	165(8)	154(5)	152(5)	123(9)		
$Ni(CO)_3[(\pi\text{-}C_5H_5Ni)_2\text{-}Ph_2PC_2Ph]$	618(7)	550(2)	532(5)	466(3)	432(7)	
	424(30)	355(25)	344(13)	332(18)	280(14)	
	262(100)	248(67)	246(84)	189(33)	187(195)	
	183(127)	178(370)	165(78)	154(220)	142(78)	
	126(166)	113(84)	107(67)	88(55)		

[a] For the complex $Ni(CO)_2(Ph_2PC{\equiv}CPh)_2$ only a very poor mass spectrum could be obtained owing to decomposition in the mass spectrometer. The remaining complexes described in this paper were too involatile for mass spectral analysis.

TABLE 5

INFRARED SPECTRA OF NICKEL COMPLEXES [a] (cm^{-1})

Compound	$\nu(C{\equiv}C)$ [b]	$\nu(CO)$		Other
$(\pi\text{-}C_5H_5Ni)_2Ph_2PC_2\text{-}t\text{-}Bu$	1550 m			
$(\pi\text{-}C_5H_5Ni)_2Ph_2P(O)C_2\text{-}t\text{-}Bu$	1550 s			1179 s, 1165 m; $\nu(P{=}O)$
$(\pi\text{-}C_5H_5Ni)_2(Ph_2P(Me)\text{-}C_2\text{-}t\text{-}Bu)I$	1531 s, 1525 (sh)			
$(\pi\text{-}C_5H_5Ni)_2(Ph_2P(Et)\text{-}C_2\text{-}t\text{-}Bu)Br$	1530 s			
$PdCl_2[(\pi\text{-}C_5H_5Ni)_2\text{-}(Ph_2PC_2\text{-}t\text{-}Bu)]_2$	1545 s, 1530 (sh)			350 m; $\nu(Pd{-}Cl)$
$Ni(CO)_2(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$	2201 m, 2160 m	1999 s	2009 s	
		1983 s	1964 s	
		1935 s	(C_6H_{12})	
		1910 (sh)	(KBr)	
$(\pi\text{-}C_5H_5Ni)_2Ph_2P(O)C_2Ph$	1558 m			1193 m, 1186 m
				1177 s, $\nu(P{=}O)$
$Ni(CO)_2(Ph_2PC{\equiv}CPh)_2$	2174	2018 s	2018 s	
		1985 (sh)	2007 (sh)	
		1950 s	2002 w	
		1920 m	1962 (C_6H_{12})	
$Ni(CO)_3[(\pi\text{-}C_5H_5Ni)_2\text{-}Ph_2PC_2Ph]$	1568 m	2060 s	2070 s	
		1993 s	1997 s	
		1984 s	(C_6H_{12})	
		1947 m		

[a] Nujol mull unless other specified. [b] Bands in the 1500—1600 cm^{-1} region are due to $\nu(C{\equiv}C)$ coordinated to nickel.

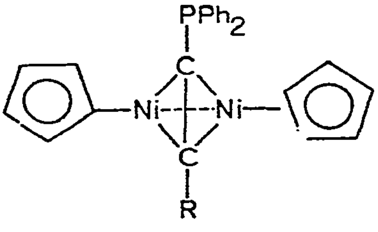
TABLE 6

NMR DATA FOR NICKEL COMPLEXES [a]

Compound	Chemical shift	Assignment
(π-$C_5H_5Ni)_2(Ph_2PC_2$-t-Bu)	7.80, 7.40 (m)	C_6H_5
	5.23 (s)	π-C_5H_5
	1.03 (s)	—$C(CH_3)_3$
(π-$C_5H_5Ni)_2(Ph_2P(O)C_2$-t-Bu)	8.10, 7.50 (m)	C_6H_5
	5.22 (s)	π-C_5H_5
	1.25	—$C(CH_3)_3$
(π-$C_5H_5Ni)_2(Ph_2P(Me)C_2$-t-Bu)I	7.80, 7.33 (m)	C_6H_5
	5.42 (s)	π-C_5H_5
	3.01, 2.80 (d) [J(P—H) 12.6 Hz]	—CH_3
	1.10 (s)	—$C(CH_3)_3$
(π-$C_5H_5Ni)_2(Ph_2P(Et)C_2$-t-Bu)Br	7.60 (m)	C_6H_5
	5.44 (s)	π-C_5H_5
	3.27, 3.15 (double quartet) [^2J(P—H) 6.0 Hz; ^3J(H—H) 3.5 Hz]	—CH_2
	2.50, 2.30 (double triplet) [^3J(P—H) 10.0 Hz; ^3J(H—H) 3.5 Hz]	—CH_3
$PdCl_2[(\pi$-$C_5H_5Ni)_2(Ph_2PC_2$-t-Bu)$]_2$	8.00, 7.47 (m)	C_6H_5
	5.03 (s)	π-C_5H_5
	1.46 (s)	—$C(CH_3)_3$
$Ni(CO)_2(PhPC{\equiv}C$-t-Bu$)_2$	7.66, 7.33 (m)	C_6H_5
	1.58 (s)	—$C(CH_3)_3$
(π-$C_5H_5Ni)_2(Ph_2P(O)C_2Ph)$	7.83 (m), 7.46 (m)	—C_6H_5
	5.13 (s)	π-C_5H_5
$Ni(CO)_2(Ph_2PC{\equiv}CPh)_2$	7.70 (m), 7.23 (m)	—C_6H_5
$Ni(CO)_3[(\pi$-$C_5H_5Ni)_2(Ph_2PC_2Ph)]$	7.70 (m), 7.33 (m)	C_6H_5
	5.16 (s)	π-C_5H_6

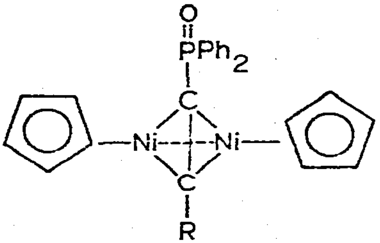
[a] At 60 MHz in $CDCl_3$ with TMS as an internal reference. s, singlet, d, doublet, m, multiplet.

cule or a neutral $Ph_2PC{\equiv}C$-t-Bu molecule to give ions at *m/e* 327, 446, 430 and 246 respectively. The ion $(\pi$-$C_5H_5Ni)_2^+$ (*m/e* 246) appears consistently in the mass spectra of binuclear π-cyclopentadienylnickel complexes and similar fragmentation mechanisms have been noted for analogous alkyne bridged π-cyclopentadienylmetal complexes [2, 18]. In the infrared spectrum ν(C≡C) of the ligand is absent but a new band of medium intensity at 1550 cm^{-1} can be assigned to ν(C≡C) of a π-coordinated acetylene [2]. The NMR spectrum (Table 6) shows singlets due to a π-cyclopentadienyl group (10 protons) and a tert-butyl group (9 protons) together with a complicated phenyl proton resonance (10 protons). The assignment of structure II containing an uncoordinated phosphorus atom, follows from the above evidence and from the quaternization of the ter-



(II)

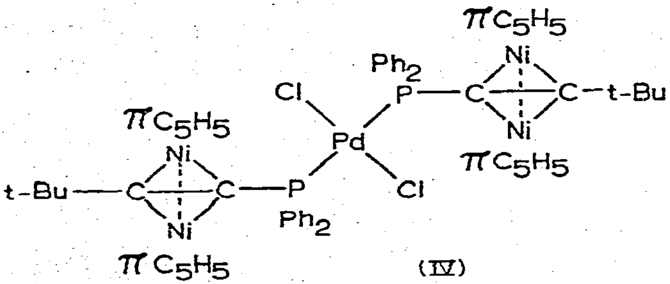
tiary phosphine in II on reaction with methyl iodide and ethyl bromide with the formation of the phosphonium salt complexes $[(\pi\text{-}C_5H_5Ni)_2(Ph_2P(R)C_2\text{-t-Bu})]X$ (R = Me, Et; X = I, Br). NMR spectra for these complexes of the cationic ligands $Ph_2P^+(R)C\equiv\text{-t-Bu}$ (R = Me, Et) show, in addition to resonances present in $(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2\text{-t-Bu})$, signals due to a P—CH$_3$ group [doublet; ^2J(P—H) 12.6 Hz] and a P—CH$_2$CH$_3$ group [double quartet ^2J(P—H) 6.0 Hz, —CH$_2$—; double triplet ^3J(P—H) 10.0 Hz, —CH$_3$; ^3J(H—H) 3.5 Hz] respectively. These complexes are apparently the first reported examples of π-complexes of phosphonium salts. The acetylene complex $(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2\text{-t-Bu})$ can be simply and effectively converted to a new compound by passage through an alumina column using benzene as an eluant. This complex which is identical with the product obtained from band 4 in the $(\pi\text{-}C_5H_5)_2Ni/Ph_2PC\equiv C\text{-t-Bu}$ reaction and band 5 in the $[(\pi\text{-}C_5H_5)Ni(CO)]_2/Ph_2PC\equiv C\text{-t-Bu}$ reaction, shows new IR bands at 1179s and 1165 cm^{-1} typical of an uncoordinated phosphine oxide [19]. Otherwise spectral data (Tables 4 and 5) point to a close structural similarity with $(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2\text{-t-Bu})$. Structure III having a π-bonded acetylenic phosphine



(III)

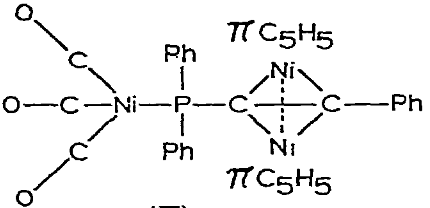
oxide ligand is assigned to this compound. An entirely analogous complex $(\pi\text{-}C_5H_5Ni)_2[Ph_2P(O)C_2Ph]$ was obtained from the nickelocene or π-cyclopentadienylnickel carbonyl dimer reactions with $Ph_2PC\equiv CPh$. Only two other organometallic acetylenic phosphine oxide complexes, $Co_2(CO)_6[(C_6F_5)_2P(O)C_2Ph]$ and $Co_2(CO)_6[Ph_2P(O)C_2\text{-t-Bu}]$ [2] have so far been described. Such compounds are of course potential donor ligands since the phosphine oxide moiety is not directly involved in complexation.

The free "phosphine" $(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2\text{-t-Bu})$ may also be used as a donor ligand. Thus reaction with *trans*-$(PhCN)_2PdCl_2$ yields the palladium bis(phosphine) complex *trans*-$PdCl_2[(\pi\text{-}C_5H_5Ni)_2Ph_2PC_2\text{-t-Bu}]_2$ of structure IV.



(IV)

Assignment of *trans* stereochemistry follows from the appearance of a single strong ν(Pd—Cl) frequency at 350 cm^{-1} in the far-infrared spectrum which can be compared with a value of 339 cm^{-1} in *trans*-$PdCl_2(Me_3P)_2$ [20] but frequencies of 300 and 316 cm^{-1} in *cis*-$PdCl_2(Ph_2PC{\equiv}C\text{-t-Bu})_2$ [21]. The availability of only small quantities of $(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2\text{-t-Bu})$ and its air sensitivity precluded further attempts to synthesize other polynuclear "phosphine" complexes of this type. In view of the isolation of $(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2\text{-t-Bu})$, it seemed somewhat surprising that no product of this type could be separated from the $Ph_2PC{\equiv}CPh$ reactions. However, organometallic phosphines of type I might be expected to react further with $[\pi\text{-}C_5H_5Ni(CO)]_2$ according to eqn. 1 or with $Ni(CO)_4$ produced via decomposition of the dimer to give trinuclear species of type V. A complex of type V (R = Ph) was indeed isolated from the $[\pi\text{-}C_5H_5\text{-}Ni(CO)]_2/Ph_2PC{\equiv}CPh$ reaction mixture. This compound exhibits $\nu(CO)$ infrared bands at 2070, 1997 cm^{-1} in cyclohexane solution typical of an $Ni(CO)_3L$ (L = phosphine) complex and a coordinated $\nu(C{\equiv}C)$ band at 1568 cm^{-1}. The NMR spectrum (Table 6) shows phenyl ring and π-cyclopentadienyl proton resonances with area ratios 15/10. Although a parent ion was not found in the mass spectrum for this high molecular weight compound, fragment ions $Ni(CO)[(\pi\text{-}C_5H_5Ni)_2Ph_2PC_2Ph]$ *m/e* 618, $(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2Ph)$ *m/e* 532, and $\pi\text{-}C_5H_5Ni_2(Ph_2PC_2C_6H_4)$ *m/e* 466 confirm the presence of the skeleton in V. Presumably $(\pi\text{-}C_5H_5Ni)_2(Ph_2PC_2Ph)$ is converted rapidly into $Ni(CO)_3[(\pi\text{-}C_5H_5\text{-}Ni)_2Ph_2PC_2Ph]$ during the reaction or to $(\pi\text{-}C_5H_5Ni)_2(Ph_2P(O)C_2Ph)$ on the column thus preventing its isolation.



(V)

Acknowledgements

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