New Nickel *o*-Methylbenzyl Complexes. Crystal and Molecular Structures of $Ni(\eta^3-CH_2C_6H_4-o-Me)Cl(PMe_3)$ and $Ni_3(\eta^1-CH_2C_6H_4-o-Me)_4(PMe_3)_2(\mu_3-OH)_2$

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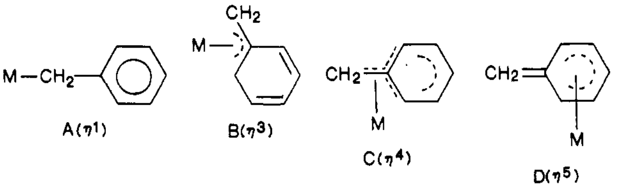
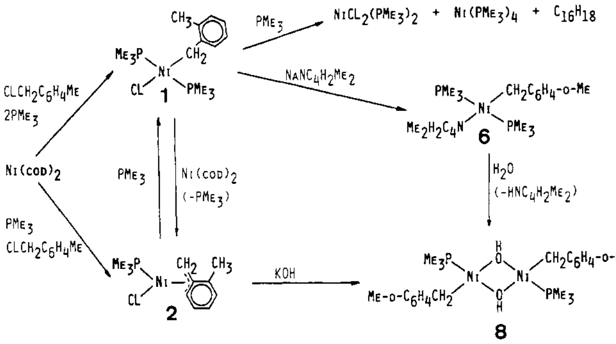
The formation and properties of the *o*-methylbenzyl complexes $Ni(\eta^1-CH_2C_6H_4-o-Me)Cl(PMe_3)_2$ (1), $Ni(\eta^3-CH_2C_6H_4-o-Me)Cl(PMe_3)$ (2), and $Ni_3(\eta^1-CH_2C_6H_4-o-Me)_4(PMe_3)_2(\mu_3-OH)_2$ (3) are reported. Alkyl 1 reacts with CO to yield the expected acyl $Ni(COR)Cl(PMe_3)_2$ (4) while metathetical replacement of the chloride ligand affords the related complexes $NiR(X)(PMe_3)_2$ (X = NCS, **5**; X = $NC_4H_2Me_2$, **6**). Interaction of the pseudoallyl 2 with KOH produces the hydroxo-bridged dimer $[NiR(PMe_3)(\mu-OH)]_2$ (**8**) which readily forms the solid-state adducts $8\cdot NHC_4H_2Me_2$ and $8\cdot 2HNC_4H_2Me_2$ when crystallized in the presence of 2,5-dimethylpyrrole. The dialkyl complexes $Ni(CH_2C_6H_4-o-Me)_2L_2$ (L = py, **12**; L_2 = tmed, **13**) have also been obtained, but attempts to isolate the PMe_3 analogue $NiR_2(PMe_3)_2$ as a crystalline solid led always to the reductive elimination products $Ni(PMe_3)_4$ and $C_{16}H_{18}$. Complexes 2 and 3 have been characterized by X-ray crystallography. 2 is monoclinic, space group $P2_1/n$, with cell dimensions a = 7.138 (2) Å, b = 17.151 (2) Å, c = 10.811 (2) Å, β = 98.45 (2)°, V = 1309.11 Å^3, and Z = 4. The molecule exhibits a distorted square-planar geometry, with the pseudoallylic *o*-methylbenzyl ligand unsymmetrically bonded to the nickel center. Crystals of 3 are triclinic, space group $P\bar{1}$, with cell dimensions a = 10.428 (3) Å, b = 12.646 (3) Å, c = 16.551 (3) Å, α = 70.68 (2)°, β = 79.54 (1)°, γ = 69.20 (2)°, V = 1920.4 Å^3, and Z = 2. The molecule consists of a distorted trigonal-bipyramidal $Ni_3(OH)_2$ core in which the Ni(II) ions are four coordinated to the two hydroxo groups and to two *o*-methylbenzyl groups for one of the Ni(II) ions and to one alkyl group and one PMe_3 ligand for the other two Ni(II) ions.

The benzyl ligand, $C_6H_5CH_2$, and other similar groups, including the closely related *o*-methylbenzyl, *o*-$CH_3C_6H_4CH_2$, differ from simple alkyl groups in their capability to adopt a variety of coordination modes ranging from the classical η^1-bonding (A) to the rather unusual η^5-bonding (D).



Scheme I. Synthesis and Chemical Properties of Complexes 1 and 2



All of these structural types have been reported in the literature[1-7] and in some cases authenticated by X-ray crystallography. The adoption of a particular coordination mode is strongly dependent on the nature of the ML_n fragment to which the benzyl-type ligand is bonded. Thus, η^1-interactions have been found[1,2] in several Pt(II) and Ni(II) complexes of composition $M(CH_2C_6H_4-o-Me)_2(PR_3)_2$, while for the related Ru(II) compounds, δ-hydrogen abstraction from the *o*-xylyl methyl group is so facile, even at low temperature, that the $\eta^2:\eta^2$-*o*-xylylene complexes $Ru(CH_2C_6H_4CH_2)(PR_3)_3$ are obtained instead of the corresponding dialkyls.[3] The η^3-coordination (B), first found in $CpMo(CH_2C_6H_5)(CO)_2$,[4] has also been demonstrated in other organometallic systems, i.e., $Rh(CH_2C_6H_4-o-Me)(PPh_3)_2$[5a] and $Zr(OAr)(CH_2Ph)_3$.[5b] On the other hand, the

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(11) A radical pathway involving homolytic cleavage of the Ni–C bond with formation of an unstable Ni(I) complex (path E in Scheme III) has been proposed[12a] for the slow decomposition of $Ni(CH_2C_6H_5)Cl(PPh_3)_2$, while disproportionation of the monoalkyl to a mixture of the dichloride an the dialkyl (F) is thought to be responsible for the formation of $NiX_2(PEt_3)_2$ complexes[12b] as byproducts of the oxidative addition of fluorohalobenzenes to $Ni(PEt_3)_4$. See also ref 12c.

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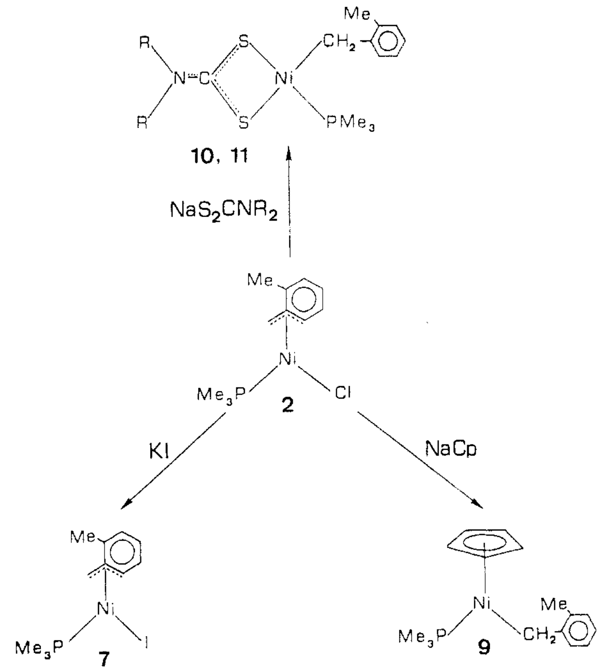
Scheme II. Some Reactions of the Pseudoallylic Complex 2



structures of the high-valent early-transition-metal benzyls[6a] $M(CH_2Ph)_4$ (M = Ti, Zr, Hf) and of the organic actinides $(\eta^5\text{-}C_5Me_5)Th(CH_2Ph)_3$[6b] and $Th(CH_2C_6H_5)_4(dmpe)_2$ and $U(CH_2C_6H_5)_3Me(dmpe)$[6c] (dmpe = $Me_2PCH_2CH_2PMe_2$) display distortions from the η^1-coordination that approach the ipso and the two ortho carbon atoms of the benzyl groups to the metal atom, yielding formally η^4-benzyl structures. Finally, the unusual η^5-bonding mode D has recently been proposed for the excited structure of $Rh(CH_2C_6Me_5)[P(O\text{-}i\text{-}C_3H_7)_3]_2$[7a] and has precedent in the structurally characterized $CpFe(\eta^5\text{-}C_6Me_5CH_2)$.[7b]

Following earlier studies from our group on the formation of nickel alkyl and acyl complexes[8] we have investigated reactions of the *o*-methylbenzyl ligand with several nickel complexes. Herein, we report the results based on reactions with $Ni(cod)_2$ (cod = 1,5-cyclooctadiene) and with several Ni(II) complexes containing phosphorus or nitrogen donor ligands that lead to the formation of η^1, A, and η^3, B, structures (Schemes I and II). We also report a rational synthesis for the trimetallic compound $Ni_3(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)_4(PMe_3)_2(\mu_3\text{-}OH)_2$, from the hydroxo-bridged species $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2$ and the dialkyl compound $Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2(tmed)$ (tmed = $Me_2NCH_2CH_2NMe_2$), in the presence of catalytic amounts of PMe_3. X-ray crystallographic studies show the trimetallic compound to consist of one NiR_2 fragment and two $Ni(R)PMe_3$ fragments joined by two triply bridging hydroxo groups. Part of this work has been reported in preliminary form.[9]

Results and Discussion

Synthesis and Properties of *trans*-$Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)_2$ (1) and $Ni(\eta^3\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)$ (2). The Crystal and Molecular Structure of 2. When the synthesis of *trans*-$Ni(CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)_2$ (1) is attempted by the classical and otherwise successful,[8] Grignard route, i.e., treatment of $NiCl_2(PMe_3)_2$ with 1 equiv of $Mg(CH_2C_6H_4\text{-}o\text{-}Me)Cl$ in Et_2O, the yellow crystalline complex 1 is formed, together with two other nickel-containing products which can also be isolated in variable amounts from the reactions mixture: a red crystalline material of analytical composition $Ni(CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)$ (2) and a dark red, nearly black, insoluble solid, identified by X-ray crystallography as the trimetallic species $Ni_3(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)_4(PMe_3)_2(\mu_3\text{-}OH)_2$ (3). As this synthetic procedure suffers from several disadvantages, including unpredictable yields, difficulties in the separation of the three complexes, and lack of reproducibility, compounds 1–3 have been individually obtained by other routes.

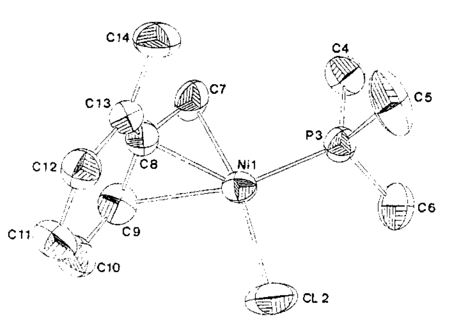


Figure 1. ORTEP diagram for 2 and atom-labeling scheme.

The halide $Me\text{-}o\text{-}C_6H_4CH_2Cl$ oxidatively adds to $Ni(cod)_2$, in the presence of stoichiometric amounts of PMe_3, with formation of 1 and 2: addition of 1 equiv of RCl and 2 equiv of PMe_3 to a cold suspension of $Ni(cod)_2$ in Et_2O produces 1 in 90% yield, while the use of only 1 equiv of PMe_3 affords 2 in ca. 70% yield (eq 1 and 2). An excess of PMe_3 during the synthesis of complex 1 must be avoided since it readily decomposes under these conditions.

$$Ni(cod)_2 + Me\text{-}o\text{-}C_6H_4CH_2Cl + 2PMe_3 \rightarrow Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)_2 + 2cod \quad (1)$$

$$Ni(cod)_2 + Me\text{-}o\text{-}C_6H_4CH_2Cl + PMe_3 \rightarrow Ni(\eta^3\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3) + 2cod \quad (2)$$

Complexes 1 and 2 are crystalline, air-sensitive materials, very soluble in common organic solvents in which they exist as monomers. NMR studies are in accord with their formulation as η^1- and η^3-*o*-methylbenzyl complexes and indicate in addition that they experience an intermolecular process, rapid on the NMR time scale, which involves PMe_3 association and dissociation. This is clearly shown by the broad features observed for the ^1H Ni–CH_2 resonances in both complexes (broad singlets) and for the ^{13}C resonances due to the CH_2 group bound to nickel and to the ipso and ortho carbon atoms also bonded to the metal atom in 2. That these exchanging processes are closely related is clearly inferred from the fact that mixtures of 1 and 2 show, at room temperature, only one set of proton resonances with chemical shift average of those corresponding to that of 1 and 2. In a preparative scale, 1 can be obtained in good yield by addition of 1 equiv of PMe_3 to solutions of 2, while the latter is formed, albeit in lower yields, by PMe_3 abstraction from 1, using $Ni(cod)_2$ (eq 3).

$$\underset{\mathbf{1}}{Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)_2} \underset{PMe_3}{\overset{Ni(cod)_2}{\rightleftarrows}} \underset{\mathbf{2}}{Ni(\eta^3\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)} \quad (3)$$

The pseudoallylic structure proposed for the *o*-methylbenzyl group in 2 has been confirmed by X-ray studies, whose results are shown, as an ORTEP perspective view, in Figure 1. The bond distances and angles are collected in Table II. The coordination geometry around nickel is distorted square-planar, with the main distorsion arising from the small C(7)–Ni–C(9) angle of 68.7 (3)°, which is obviously imposed by the small bite size of the η^3-*o*-methylbenzyl ligand. This small angle is compensated for by the opening of the other angles around the nickel

Table I. Summary of Crystal Data

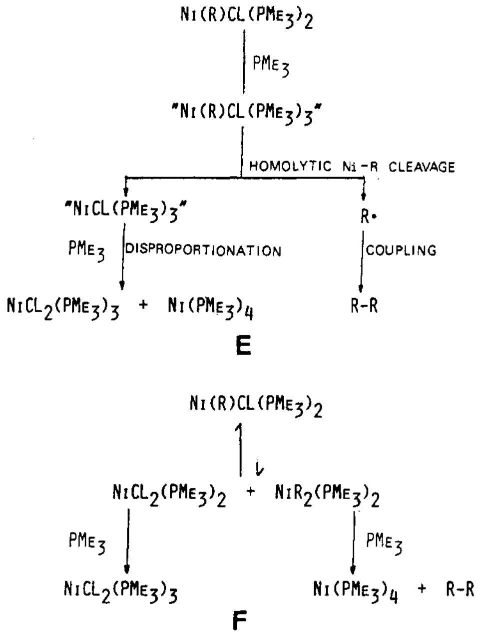
	2	3
empirical formula	$C_{11}ClH_{18}NiP$	$C_{38}H_{56}Ni_3O_2P_2$
color	red	dark red
space group	$P2_1/n^a$	$P\bar{1}$
cell dimens		
a, Å	7.138 (2)	10.428 (2)
b, Å	17.151 (2)	12.646 (3)
c, Å	10.811 (2)	16.551 (3)
α, deg		70.68 (2)
β, deg	98.45 (2)	79.54 (1)
γ, deg		69.20 (2)
Z	4	2
V, Å^3	1309.1	1920.4
D_{calcd}, g cm^{-1}	1.40	1.35
wavelength, Å	0.71069	0.71069
temp, °C	20	20
mol wt	275.39	782.5
linear abs coeff, cm^{-1}	17.72	15.64
2θ range, deg	2–60	4–50
unique data	4161	6817
data with $[I \geq 3\sigma(I)]$	1476	1983
R(*F*)	0.053	0.044
$R_w(F)$	0.060	0.050

[a] Nonstandard setting of $P2_1/c$ (No. 14).

Table II. Bond Distances (Å) and Angles (deg) for $Ni(\eta^3-CH_2C_6H_4-o-Me)Cl(PMe_3)$ (2)

Bond Distances			
Ni(1)–Cl(2)	2.189 (2)	C(7)–C(8)	1.44 (1)
Ni(1)–P(3)	2.128 (2)	C(8)–C(9)	1.39 (1)
Ni(1)–C(7)	1.930 (8)	C(9)–C(10)	1.41 (1)
Ni(1)–C(8)	2.050 (8)	C(10)–C(11)	1.35 (1)
Ni(1)–C(9)	2.318 (9)	C(11)–C(12)	1.40 (1)
P(3)–C(4)	1.79 (1)	C(12)–C(13)	1.38 (1)
P(3)–C(5)	1.82 (1)	C(13)–C(14)	1.49 (1)
P(3)–C(6)	1.810 (9)	C(13)–C(8)	1.43 (1)
Bond Angles			
Cl(2)–Ni(1)–P(3)	99.5 (1)	C(7)–C(8)–C(9)	117.1 (8)
Cl(2)–Ni(1)–C(7)	166.6 (3)	C(7)–C(8)–C(13)	123.3 (8)
Cl(2)–Ni(1)–C(8)	124.8 (2)	C(9)–C(8)–C(13)	118.3 (7)
Cl(2)–Ni(1)–C(9)	98.5 (2)	C(8)–C(9)–C(10)	121.5 (7)
P(3)–Ni(1)–C(7)	93.8 (3)	C(9)–C(10)–C(11)	119.5 (8)
P(3)–Ni(1)–C(8)	131.8 (2)	C(10)–C(11)–C(12)	120.3 (8)
P(3)–Ni(1)–C(9)	160.4 (2)	C(11)–C(12)–C(13)	121.8 (8)
C(7)–Ni(1)–C(8)	42.2 (3)	C(12)–C(13)–C(14)	120.4 (7)
C(7)–Ni(1)–C(9)	68.6 (3)	C(8)–C(13)–C(14)	120.9 (7)
C(8)–Ni(1)–C(9)	36.6 (3)		
C(4)–P(3)–C(5)	103.9 (6)		
C(4)–P(3)–C(6)	102.3 (5)		
C(5)–P(3)–C(6)	101.1 (5)		

Scheme III. Possible Pathways for the Reaction of 1 with PMe_3



center so that the sum of the angles is 360.5°. The Ni–Cl and Ni–P bond lengths have normal values (2.189 (2) and 2.128 (2) Å, respectively), similar to those found in related nickel complexes.[8a,c]

Not unexpectedly, the pseudoallylic coordination of the *o*-methylbenzyl ligand is unsymmetrical, with the strongest interaction corresponding to the methylene carbon atom (Ni–C(7) = 1.930 (8) Å) and the weakest one to the ortho carbon atom (Ni–C(9) = 2.318 (9) Å). The difference between these bond lengths, 0.388 Å, is appreciably longer than that found in the related complexes $Rh(\eta^3-CH_2C_6H_4-o-Me)(PPh_3)_2$ (0.146 Å[5a]) and $CpMo(\eta^3-CH_2C_6H_4-o-Me)(CO)_2$ (0.21 Å[4]) but much shorter than the corresponding difference in some mixed benzyl–aryloxy derivatives of Zr(IV) (0.66–0.90 Å) for which a week pseudoallylic interaction, approaching η^3-coordination, has been postulated.[5b] The *o*-methylbenzyl ligand shows appreciable distortion from planarity, since the methylene carbon is located about 0.2 Å underneath the aromatic ring, which is planar to within 0.03 Å. The C–C bond distances in the aromatic ring clearly indicate that the coordination of the *o*-xylyl ligand takes place via the ortho-unsustituted carbon atom (Table II). In agreement with this, the values found for the C(8)–C(13), C(9)–C(10), and C(11)–C(12) bond distances are considerably longer (1.41 (1) Å (average)) than those corresponding to C(10)–C(11) and C(12)–C(13), which have more double-bond character (1.36 (1) Å (average)).

Some Chemical Properties of 1 and 2. The complex $Ni(\eta^1-CH_2C_6H_4-o-Me)Cl(PMe_3)_2$ (1) displays a reaction chemistry very similar to that exhibited by other *trans*-$NiR(Cl)(PMe_3)_2$ complexes (Scheme I). Thus, it reacts with CO (20 °C, 1 atm), with quantitative formation of the expected acyl $Ni(COR)Cl(PMe_3)_2$ (4) while with KNCS or $NaNC_4H_2Me_2$-2,5 the substitution products $Ni(CH_2C_6H_4-o-Me)X(PMe_3)_2$ (X = NCS, 5; X = $NC_4H_2Me_2$, 6) are obtained. Somewhat unexpected however is the reaction with an excess of PMe_3 (5 equiv) which yields a dark blue microcrystalline precipitate of $NiCl_2(PMe_3)_3$,[10] together with $Ni(PMe_3)_4$ and $C_{16}H_{18}$ (1,2-bis(2-methylphenyl)ethane), as shown in eq 4. Of the two possible

$$Ni(CH_2C_6H_4-o-Me)Cl(PMe_3)_2 + 5PMe_3 \rightarrow NiCl_2(PMe_3)_3 + Ni(PMe_3)_4 + C_{16}H_{18} \quad (4)$$

pathways (E and F, Scheme III), which can be envisaged for this transformation,[11] we favor the latter, namely, the reversible redistribution of $NiR(Cl)P_2$ to $NiCl_2P_2$ plus NiR_2P_2, followed by the irreversible reaction of these compounds with PMe_3 to yield the observed products, on the basis that (i) an equimolar mixture of $NiCl_2P_2$ and in situ generated NiR_2P_2 (see below) readily conproportionates to the monoalkyl complex $NiR(Cl)P_2$ (ca. 70% yield) and (ii) the dialkyl complex NiR_2P_2 decomposes quickly in the presence of PMe_3 with formation of $Ni(PMe_3)_4$ and $C_{16}H_{18}$.

Attention has preferentially been paid to the chemical reactivity of the pseudoallylic species 2 (Scheme II). Metathetical replacement of the chloride ligand with KI gives the iodide complex $Ni(\eta^3-CH_2C_6H_4-o-Me)I(PMe_3)$ (7), which can be isolated as green-red dicroic crystals, with spectroscopic properties very similar to those of the chloride analogue 2. In contrast, nucleophilic displacement of Cl^- by OH^- affords the yellow-orange hydroxo-bridged species $[Ni(CH_2C_6H_4-o-Me)(PMe_3)(\mu-OH)]_2$ (8) which ex-

Table III. Bond Distances (Å) and Angles (deg) for $Ni_3(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)_4(PMe_3)_2(\mu_3\text{-}OH)_2$ (3)

Bond Angles (A) Coordination around Ni					
O(6)-Ni(1)-O(7)	70.1 (3)	O(6)-Ni(2)-O(7)	73.0 (3)	O(6)-N(13)-O(7)	71.9 (3)
O(6)-Ni(1)-C(8)	99.3 (5)	O(6)-Ni(2)-C(24)	97.8 (5)	O(6)-Ni(3)-C(32)	168.8 (5)
O(6)-Ni(1)-C(16)	170.4 (5)	O(6)-Ni(2)-P(4)	171.6 (3)	O(6)-Ni(3)-P(5)	100.7 (3)
O(7)-Ni(1)-C(8)	168.3 (5)	O(7)-Ni(2)-C(24)	170.7 (5)	O(7)-Ni(3)-C(32)	97.0 (5)
O(7)-Ni(1)-C(16)	100.5 (5)	O(7)-Ni(2)-P(4)	99.4 (3)	O(7)-Ni(3)-P(5)	172.1 (3)
C(8)-Ni(1)-C(16)	90.1 (6)	P(4)-Ni(2)-C(24)	89.6 (5)	P(5)-Ni(3)-C(32)	90.4 (4)
Ni(1)-O(6)-H(59)	123.2	Ni(1)-O(7)-H(60)	115.1		
Ni(2)-O(6)-H(59)	126.1	Ni(2)-O(7)-H(60)	133.8		
Ni(3)-O(6)-H(59)	127.7	Ni(3)-O(7)-H(60)	127.6		
(B) Phosphine and Xylyl Groups					
Ni(2)-P(4)-C(40)	118.2 (6)	C(43)-P(5)-C(44)	101.5 (7)		
Ni(2)-P(4)-C(41)	114.9 (5)	C(43)-P(5)-C(45)	103.1 (7)		
Ni(2)-P(4)-C(42)	114.1 (5)	C(44)-P(5)-C(45)	104.4 (8)		
Ni(3)-P(5)-C(43)	114.1 (5)	Ni(1)-C(8)-C(9)	115.0 (9)		
Ni(3)-P(5)-C(44)	116.8 (6)	Ni(1)-C(16)-C(17)	117 (1)		
Ni(3)-P(5)-C(45)	115.0 (5)	Ni(2)-C(24)-C(24)	112 (1)		
C(40)-P(4)-C(41)	103.0 (7)	Ni(3)-C(32)-C(33)	112.0 (9)		
C(40)-P(4)-C(42)	101.6 (8)				
C(41)-P(4)-C(42)	102.9 (7)				
ring bonded to C(8): C-C-C(av)	120 (2)				
ring bonded to C(16): C-C-C(av)	120 (2)				
ring bonded to C(24): C-C-C(av)	121 (2)				
ring bonded to C(32): C-C-C(av)	120 (2)				
(C) NonBonded Atoms					
H(59)-O(6)-O(7)	178.2	H(60)-O(7)-O(6)	169.6		
Bond Distances (A) Coordination around the Ni Atoms					
Ni(1)-O(6)	1.995 (8)	Ni(2)-P(4)	2.106 (4)	Ni(3)-P(5)	2.114 (4)
Ni(1)-O(7)	2.004 (8)	Ni(2)-O(6)	1.906 (9)	Ni(3)-O(6)	1.975 (8)
Ni(1)-C(8)	1.95 (1)	Ni(2)-O(7)	1.956 (8)	Ni(3)-O(7)	1.940 (8)
Ni(1)-C(16)	1.95 (1)	Ni(2)-C(24)	1.94 (1)	Ni(3)-C(32)	1.96 (1)
O(6)-H(59)	1.12	O(7)-H(60)	1.09		
(B) Phosphine Groups and Carbon Rings					
P(4)-C(40)	1.82 (1)	C(14)-C(15)	1.50 (2)	C(27)-C(28)	1.37 (2)
P(4)-C(41)	1.82 (1)	C(16)-C(17)	1.47 (2)	C(28)-C(29)	1.37 (2)
P(4)-C(42)	1.81 (2)	C(17)-C(18)	1.39 (2)	C(29)-C(30)	1.37 (2)
P(5)-C(43)	1.81 (1)	C(17)-C(22)	1.39 (2)	C(30)-C(31)	1.50 (2)
P(5)-C(44)	1.82 (1)	C(18)-C(19)	1.41 (3)	C(32)-C(33)	1.49 (2)
P(5)-C(45)	1.79 (2)	C(19)-C(20)	1.36 (3)	C(33)-C(34)	1.39 (2)
C(8)-C(9)	1.47 (2)	C(20)-C(21)	1.33 (3)	C(33)-C(38)	1.40 (2)
C(9)-C(10)	1.40 (2)	C(21)-C(22)	1.33 (2)	C(34)-C(35)	1.38 (2)
C(9)-C(14)	1.41 (2)	C(22)-C(23)	1.48 (2)	C(35)-C(36)	1.39 (2)
C(10)-C(11)	1.36 (2)	C(24)-C(25)	1.49 (2)	C(36)-C(37)	1.36 (2)
C(11)-C(12)	1.36 (2)	C(25)-C(26)	1.40 (2)	C(37)-C(38)	1.36 (2)
C(12)-C(13)	1.40 (2)	C(25)-C(30)	1.42 (2)	C(38)-C(39)	1.50 (2)
C(13)-C(14)	1.37 (2)	C(26)-C(27)	1.35 (2)		
(C) Nonbonded Atoms					
Ni(1)-Ni(2)	2.751 (2)	Ni(2)-Ni(3)	2.752 (2)		
Ni(1)-Ni(3)	2.763 (2)	O(6)-O(7)	2.30 (1)		

ists in solution only as the trans isomer.[13] The greater tendency of the OH^- group, as compared to Cl^- and I^-, to act as a bridging ligand, is clearly responsible for the formation of this dimeric species. Rather interestingly, compound 8 reacts with CO (20 °C, 1 atm) to produce *o*-tolylacetic acid $Me\text{-}o\text{-}C_6H_4CH_2CO_2H$ as shown in eq 5. Presumably, this reaction proceeds through an acyl–hydroxo intermediate,[14] which in the presence of CO reductively eliminates the carboxylic acid.

$$[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2 + 8CO \rightarrow 2Ni(CO)_3PMe_3 + 2Me\text{-}o\text{-}C_6H_4CH_2CO_2H \quad (5)$$

Treatment of 2 with the sodium salt of 2,5-dimethylpyrrole, $NaNC_4H_2Me_2$, produces a brown crystalline material identified as the 2,5-dimethylpyrrole adduct of 8, $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2\cdot HNC_4H_2Me_2$. It is evident that adventitious water plays an important role in this reaction, and in agreement with that, the yield of the above adduct becomes insignificant when the reaction is carried out with rigorous exclusion of water. The reaction occurs likely through a nickel–pyrrolyl derivative having a Ni–N bond extremely prone to hydrolytic cleavage by water, and this assumption finds support in the observation that the above described pyrrolyl complex $Ni(CH_2C_6H_4\text{-}o\text{-}Me)(NC_4H_2Me_2)(PMe_3)_2$ (6) decomposes readily, in the presence of water, to the same hydroxo species 8 (eq 6). It is worth noting at this point that the

$$2Ni(CH_2C_6H_4\text{-}o\text{-}Me)(NC_4H_2Me_2)(PMe_3)_2 + 2H_2O \rightarrow [Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)_2]_2 + 2HNC_4H_2Me_2 + 2PMe_3 \quad (6)$$

dinuclear complex 8 readily forms solid-state adducts when crystallized in the presence of 2,5-dimethylpyrrole. These adducts, which contain one or two molecules of pyrrole per molecule of the nickel complex, can reproducibly be in-

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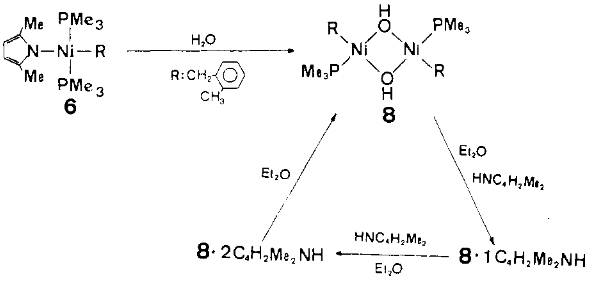
[13] This complex is a new member of a known series of hydroxo complexes of Ni(II), which generally exist in solution as a mixture of cis and trans isomers. Unpublished results from this laboratory and: Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1973**, *106*, 1433.

[14] Related acyl(aryloxy)nickel(II) complexes undergo facile reductive elimination of esters. See: Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130.

Table IV. Fractional Coordinates for $Ni(\eta^3\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)$

atom	*x/a*	*y/b*	*z/c*	*U*(iso), Å^2
Ni(1)	−0.0682 (1)	0.0593 (1)	0.1769 (1)	0.0398
Cl(2)	0.2200 (3)	0.1012 (2)	0.2402 (3)	0.0656
P(3)	−0.2063 (3)	0.1683 (1)	0.1370 (2)	0.0443
C(4)	−0.0657 (16)	0.2413 (6)	0.0751 (12)	0.0787
C(5)	−0.2715 (16)	0.2141 (6)	0.2767 (9)	0.0701
C(6)	−0.4278 (13)	0.1746 (6)	0.0317 (8)	0.0597
C(7)	−0.2979 (13)	0.0001 (5)	0.1346 (8)	0.0518
C(8)	−0.1694 (11)	−0.0479 (5)	0.2164 (7)	0.0422
C(9)	−0.0053 (13)	−0.0724 (5)	0.1723 (7)	0.0500
C(10)	0.1440 (14)	−0.1085 (6)	0.2518 (9)	0.0578
C(11)	0.1286 (12)	−0.1195 (6)	0.3734 (8)	0.0526
C(12)	−0.0325 (12)	−0.0936 (5)	0.4213 (7)	0.0465
C(13)	−0.1811 (10)	−0.0579 (5)	0.3464 (7)	0.0405
C(14)	−0.3499 (12)	−0.0299 (6)	0.4008 (9)	0.0577
H(1)	0.0070	−0.0640	0.0823	0.0500
H(2)	0.2605	−0.1261	0.2181	0.0500
H(3)	0.2325	−0.1464	0.4297	0.0500
H(4)	−0.0398	−0.1010	0.5121	0.0500
H(5)	−0.4141	0.0193	0.1666	0.0500
H(6)	−0.3319	−0.0173	0.0459	0.0500
H(7)	−0.4428	−0.0053	0.3332	0.0500
H(8)	−0.4107	−0.0749	0.4381	0.0500
H(9)	−0.3090	0.0093	0.4670	0.0500
H(10)	−0.0231	0.2212	−0.0029	0.0500
H(11)	−0.1431	0.2896	0.0556	0.0500
H(12)	0.0472	0.2537	0.1383	0.0500
H(13)	−0.1592	0.2147	0.3440	0.0500
H(14)	−0.3146	0.2683	0.2571	0.0500
H(15)	−0.3763	0.1837	0.3058	0.0500
H(16)	−0.5192	0.1359	0.0576	0.0500
H(17)	−0.4814	0.2283	0.0348	0.0500
H(18)	−0.4048	0.1623	−0.0554	0.0500

Scheme IV. Formation of 8 and Its 2,5-Dimethylpyrrole Adducts



terconverted under the conditions summarized in Scheme IV. Despite the complete dissociation experienced by these adducts in solution, as demonstrated by ^{1}H and ^{13}C NMR studies, an X-ray analysis carried out on $8\cdot HNC_4H_2Me_2$ reveals a symmetric interaction in the solid state between the OH ligands and the pyrrole N–H group.[15]

Finally, it should be mentioned that NaCp reacts cleanly with **2** with formation of a green complex, identified as $CpNi(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)$ (**9**) while the dialkyldithiocarbamates $R_2NCS_2^-$ (R = Me, i-Pr) produce the 16-electron species $Ni(CH_2C_6H_4\text{-}o\text{-}Me)(S_2CNR_2)(PMe_3)$ (R = Me, **10**; R = *i*-Pr, **11**). Variable-temperature ^{1}H NMR studies for these dithiocarbamate complexes show the existence of a process that interchanges the alkyl groups of the S_2CNR_2 ligand by an intermolecular mechanism similar to that observed previously for other $NiR(S_2CNR'_2)(PMe_3)$ complexes.[16]

Bis(*o*-methylbenzyl) Complexes. A few years ago, we reported[8b,c] the synthesis of several dialkyl complexes of Ni(II), stabilized by P-containing mono- and bidentate ligands. Since these complexes cannot be made by alkylation of $NiCl_2(PR_3)_2$ compounds, advantage was taken of the facility with which the unstable derivatives $Ni(CH_2SiMe_3)_2L_2$ (L = py; L_2 = tmed) lose in solution the N-containing ligands, particularly in the presence of tertiary phosphines. It was noted that while the N-containing products were unstable in solution in the absence of an excess of the free base, the phosphine derivatives were much more stable and would not decompose when kept under nitrogen, even in the absence of the free ligand. Rather surprisingly, the bis(*o*-methylbenzyl) complexes display a different behavior.

Treatment of $NiCl_2(py)_4$ with 2 equiv of $Mg(CH_2C_6H_4\text{-}o\text{-}Me)Cl$ in the presence of an excess of pyridine or tmed produces, albeit in low yields, dark red crystalline complexes of composition $Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2L_2$ (L = py, **12**; L_2 = tmed, **13**). Both compounds are very soluble in nonpolar organic solvents, and the resulting solutions are stable at room temperature for several days when kept under dinitrogen. Although the molecular geometry of the pyridine complex **12** cannot be ascertained from the available IR and ^{13}C NMR data, a cis distribution is proposed by similarity with the structurally characterized *cis*-$Ni(CH_2SiMe_3)_2(py)_2$.[8b]

Attempts have been made to obtain the trimethylphosphine derivative $Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2(PMe_3)_2$ by a similar procedure, i.e., treatment of $NiCl_2(py)_4$ with Mg(R)Cl in the presence of PMe_3 and by addition of an excess of PMe_3 to the dialkyl **12**. Nevertheless only the reductive elimination products $Ni(PMe_3)_4$ and $C_{16}H_{18}$ are obtained by either route, and this may be related to the tendency of $Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2(PMe_3)_2$ to undergo a reductive elimination process induced by free PMe_3. To avoid this reaction, the bis(phosphine) complex was generated by reacting either of the dialkyl **12** or **13** with 1.8 equiv of PMe_3, and although the desired $NiR_2(PMe_3)_2$ was formed in solution,[17] only the reductive elimination products and the trimetallic species $Ni_3(CH_2C_6H_4\text{-}o\text{-}Me)_4(PMe_3)_2(\mu_3\text{-}OH)_2$ (**3**) could be isolated from the reaction mixture. As discussed below, the formation of the latter compound requires the participation of $NiR_2(PMe_3)_2$ and of small amounts of water. It seems therefore reasonable that our failure to isolate this complex in crystalline form is due to its tendency to undergo reductive elimination combined with its high solubility and its sensitivity toward water.[18]

The Formation of $Ni_3(CH_2C_6H_4\text{-}o\text{-}Me)_4(PMe_3)_2(\mu_3\text{-}OH)_2$ (3): A Rational Synthetic Route and Its Molecular Structure. As already mentioned, complex **3** is formed, together with **1** and **2**, in the reaction of $NiCl_2(PMe_3)_2$ and $Mg(CH_2C_6H_4\text{-}o\text{-}Me)Cl$. This air-sensitive complex appears only at the later stages of the workup procedure, and its formation is possibly due to the action of adventitious water on some species formed in the course of the reaction. The presence of hydroxo ligands in the molecules of **3** is revealed by the appearance of an IR absorption at 3570 cm^{-1}.

Complex **3** is stable as a solid when kept under nitrogen, but it decomposes in solution, even under inert atmosphere. This and its very low solubility have precluded

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(15) Marín, J. M., unpublished results.

(16) Carmona, E.; González, F.; Poveda, M. L.; Marín, J. M. *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 185.

(17) Evidence for this comes from the following: (i) $Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2(PMe_3)_2$, in situ generated by addition of a slight defect of PMe_3 to complexes **12** or **13**, reacts with equimolar amounts of $NiCl_2(PMe_3)_2$ to afford the conproportionation product $NiCl(R)(PMe_3)_2$ in high yield (70%); (ii) $NiR_2(PMe_3)_2$, formed as above, reacts with equimolar amounts of $[NiR(PMe_3)(\mu\text{-}OH)]_2$, with formation of the trimetallic species **3** (see text).

(18) Note that 2 mmol of water can decompose up to 5 mmol of $NiR_2(PMe_3)_2$: $5NiR_2(PMe_3)_2 + 2H_2O \rightarrow Ni_3R_4(PMe_3)_2(\mu_3\text{-}OH)_2 + 2Ni(PMe_3)_4 + 2R\text{–}R + 2R\text{–}H$.

Table V. Fractional Coordinates for $Ni_3(CH_2C_6H_4Me\text{-}o)_4(PMe_3)_2(\mu_3\text{-}OH)_2$

atom	*x*/*a*	*y*/*b*	*z*/C	*U*(iso), Å^2
Ni(1)	0.0081 (2)	0.2238 (2)	0.2407 (1)	0.0410
Ni(2)	0.1634 (2)	0.3696 (2)	0.2161 (1)	0.0368
Ni(3)	0.2791 (2)	0.1290 (2)	0.2818 (1)	0.0372
P(4)	0.1183 (4)	0.5060 (3)	0.2732 (3)	0.0460
P(5)	0.4387 (4)	0.0061 (3)	0.2294 (2)	0.0444
O(6)	0.1862 (8)	0.2374 (7)	0.1774 (5)	0.0360
O(7)	0.1203 (8)	0.2478 (7)	0.3155 (5)	0.0384
C(8)	−0.0747 (14)	0.2068 (15)	0.1513 (10)	0.0525
C(9)	0.0203 (14)	0.1328 (14)	0.0997 (10)	0.0399
C(10)	0.0720 (15)	0.1807 (13)	0.0169 (11)	0.0487
C(11)	0.1553 (15)	0.1128 (15)	−0.0332 (10)	0.0533
C(12)	0.1905 (15)	−0.0066 (16)	−0.0040 (11)	0.0550
C(13)	0.1457 (15)	−0.0593 (13)	0.0802 (12)	0.0519
C(14)	0.0628 (14)	0.0088 (14)	0.1308 (10)	0.0455
C(15)	0.0161 (17)	−0.0489 (15)	0.2209 (11)	0.0761
C(16)	−0.1512 (15)	0.2072 (16)	0.3196 (10)	0.0613
C(17)	−0.1919 (15)	0.2746 (15)	0.3829 (10)	0.0429
C(18)	−0.1543 (15)	0.2195 (17)	0.4670 (14)	0.0666
C(19)	−0.2025 (22)	0.2794 (26)	0.5300 (11)	0.0791
C(20)	−0.2819 (23)	0.3951 (27)	0.5054 (16)	0.0815
C(21)	−0.3153 (18)	0.4483 (19)	0.4244 (16)	0.0814
C(22)	−0.2702 (16)	0.3934 (16)	0.3637 (11)	0.0541
C(23)	−0.3101 (19)	0.4566 (19)	0.2745 (13)	0.0992
C(24)	0.2065 (15)	0.4738 (13)	0.1069 (9)	0.0503
C(25)	0.3076 (15)	0.4075 (13)	0.0506 (9)	0.0475
C(26)	0.2669 (17)	0.3865 (15)	−0.0176 (10)	0.0517
C(27)	0.3558 (22)	0.3276 (17)	−0.0706 (11)	0.0697
C(28)	0.4939 (21)	0.2870 (15)	−0.0611 (11)	0.0693
C(29)	0.5378 (16)	0.3071 (14)	0.0039 (12)	0.0615
C(30)	0.4519 (17)	0.3653 (14)	0.0593 (9)	0.0529
C(31)	0.5047 (15)	0.3832 (15)	0.1306 (11)	0.0697
C(32)	0.3411 (14)	0.0393 (13)	0.3972 (9)	0.0480
C(33)	0.3146 (14)	0.1174 (12)	0.4531 (9)	0.0401
C(34)	0.2049 (16)	0.1219 (15)	0.5149 (10)	0.0568
C(35)	0.1756 (16)	0.1899 (17)	0.5698 (10)	0.0587
C(36)	0.2577 (17)	0.2579 (16)	0.5642 (10)	0.0598
C(37)	0.3656 (16)	0.2535 (13)	0.5036 (10)	0.0485
C(38)	0.3953 (13)	0.1877 (12)	0.4482 (9)	0.0394
C(39)	0.5154 (15)	0.1889 (14)	0.3828 (10)	0.0559
C(40)	0.2554 (17)	0.5634 (15)	0.2734 (10)	0.0707
C(41)	0.0541 (14)	0.4710 (12)	0.3852 (9)	0.0504
C(42)	−0.0143 (18)	0.6396 (14)	0.2237 (11)	0.0705
C(43)	0.4316 (13)	0.0311 (13)	0.1157 (9)	0.0510
C(44)	0.6138 (14)	0.0018 (15)	0.2335 (10)	0.0611
C(45)	0.4425 (17)	−0.1447 (14)	0.2752 (10)	0.0726
H(1)	0.0457	0.2718	−0.0077	0.0500
H(2)	0.1912	0.1528	−0.0938	0.0500
H(3)	0.2498	−0.0584	−0.0428	0.0500
H(4)	0.1757	−0.1504	0.1044	0.0500
H(6)	−0.0901	0.1328	0.4843	0.0500
H(7)	−0.1810	0.2392	0.5939	0.0500
H(8)	−0.3179	0.4447	0.5479	0.0500
H(9)	−0.3780	0.5360	0.4062	0.0500
H(11)	0.1631	0.4173	−0.0273	0.0500
H(12)	0.3185	0.3136	−0.1187	0.0500
H(13)	0.5624	0.2431	−0.1019	0.0500
H(14)	0.6419	0.2763	0.0115	0.0500
H(16)	0.1424	0.0722	0.5199	0.0500
H(17)	0.0929	0.1903	0.6149	0.0500
H(18)	0.2384	0.3100	0.6045	0.0500
H(19)	0.4291	0.3021	0.4997	0.0500
H(21)	−0.1167	0.2898	0.1104	0.0500
H(22)	−0.1511	0.1700	0.1798	0.0500
H(23)	−0.1297	0.1190	0.3531	0.0500
H(24)	−0.2331	0.2336	0.2835	0.0500
H(25)	0.2466	0.5306	0.1181	0.0500
H(26)	0.1170	0.5213	0.0761	0.0500
H(27)	0.4446	−0.0050	0.3923	0.0500
H(28)	0.2886	−0.0213	0.4251	0.0500
H(29)	0.2996	0.5863	0.2166	0.0500
H(30)	0.2156	0.6370	0.2950	0.0500
H(31)	0.3290	0.4997	0.3127	0.0500
H(32)	0.1225	0.3953	0.4201	0.0500
H(33)	0.0422	0.5400	0.4091	0.0500
H(34)	−0.0399	0.4584	0.3904	0.0500
H(35)	−0.1000	0.6192	0.2198	0.0500
H(36)	−0.0408	0.6975	0.2602	0.0500
H(37)	0.0213	0.6789	0.1630	0.0500
H(38)	0.3356	0.0357	0.1042	0.0500
H(39)	0.4499	0.1095	0.0816	0.0500
H(40)	0.5050	−0.0373	0.0965	0.0500
H(41)	0.6207	0.0856	0.2081	0.0500
H(42)	0.6392	−0.0314	0.2964	0.0500
H(43)	0.6803	−0.0522	0.1985	0.0500
H(44)	0.4469	−0.1685	0.3408	0.0500
H(45)	0.5283	−0.1987	0.2496	0.0500
H(46)	0.3554	−0.1542	0.2617	0.0500
H(47)	−0.0454	0.0156	0.2492	0.0500
H(48)	0.1004	−0.0997	0.2559	0.0500
H(49)	−0.0393	−0.1012	0.2196	0.0500
H(50)	−0.2672	0.4009	0.2361	0.0500
H(51)	−0.2775	0.5293	0.2505	0.0500
H(52)	−0.4164	0.4835	0.2739	0.0500
H(53)	0.4234	0.4287	0.1647	0.0500
H(54)	0.5723	0.4306	0.1055	0.0500
H(55)	0.5545	0.3021	0.1712	0.0500
H(56)	0.5222	0.1350	0.3463	0.0500
H(57)	0.6045	0.1593	0.4135	0.0500
H(58)	0.5019	0.2741	0.3434	0.0500
H(59)	0.2150	0.2325	0.1101	0.0500
H(60)	0.0741	0.2470	0.3802	0.0500

its characterization by NMR methods. Nevertheless, good quality crystals of this complex can be obtained, and this allows determination of its molecular complexity by X-ray techniques.

Figure 2 shows an ORTEP view of **3** including the atom numbering scheme. The structure of this complex may be described as consisting of a central core formed by a triangular array of metal atoms and two hydroxo groups that unsymmetrically bridge the edges of the nearly equilateral Ni_3 triangle. This geometrical distribution of the metal ions and the hydroxo ligands resembles that recently found for the $Cu_3(OH)_2$ central unit of a Cu(II) cryptate containing a tritopic hexaazamacrocycle.[19] The two $M_3(OH)_2$ cores have distorted trigonal-bipyramidal geometry, with the three M(II) ions in the equatorial plane, at the relatively long separation of 2.75 (4) Å (M = Ni) and 2.808 (3) Å (M = Cu). The M···M distance in the nickel complex, while shorter than that found in other triangular $Ni_3(OH)$ cores (ca. 3.04–3.14 Å[20]) and in some diamagnetic $Ni_3(\mu_3\text{-}S)_2$ phosphine-containing compounds (~2.95 Å[21]), is considerably longer than that observed in metal–metal bonded trinuclear organometallic compounds of nickel.[22] This indicates no or very weak Ni···Ni bonding interaction. As in the related complex $Cp_3Ni_3S_2$,[23] the relatively small intramolecular O(6)···O(7) distance at 2.30 (1) Å and the appreciably acute O–Ni–O angle (72 (1)° (average)) may be due to a compression of the Ni_3O_2 skeleton due to the long Ni···Ni distances, motivated by the absence of metal–metal interaction. That this is not the only factor governing the structures of these complexes is clearly shown by the fact that, in the above-mentioned $Cu_3(OH)_2$ cluster, the longer Cu···Cu distances lead to a longer O···O

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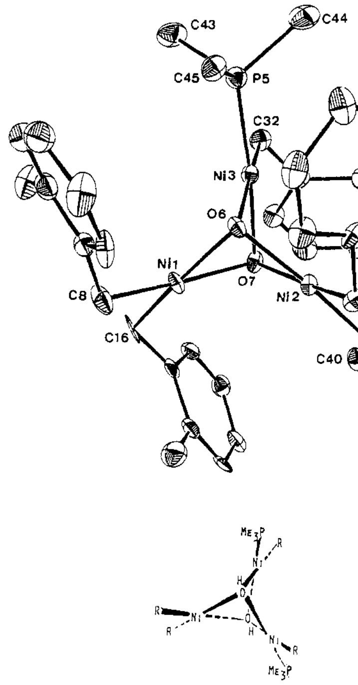


Figure 2. Molecular structure of 3 and atom-labeling scheme. The C_6H_4Me labels have been omitted for clarity.

separation. This is a consequence of the similar values found for the O–M–O angles in both complexes.

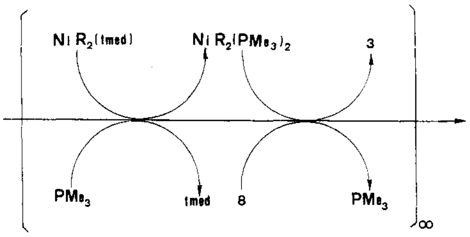
Complex **3** can be viewed as formed by three square-planar nickel(II) moieties which share the two hydroxo groups, each coordination plane being approximately perpendicular to the Ni_3 triangle and bisecting the corresponding Ni–Ni–Ni angle. In an alternative description the molecules of **3** can be described as consisting of a $Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2$ fragment stabilized by coordination to the OH groups of the binuclear hydroxo-bridged species $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH]_2$ (**8**). Hence, apart from the two hydroxo ions, the coordination sphere around the nickel ions is completed by an alkyl ligand and a PMe_3 group for Ni(2) and Ni(3) and by two alkyl groups for Ni(1). In accord with the above, Ni(1) exhibits the longest Ni···O separations (1.995 (8) and 2.004 (8) Å for O(6) and O(7), respectively) while for the other Ni(II) ions, the Ni–O(6) and Ni–O(7) distances are 1.906 (9) and 1.956 (8) Å for Ni(2) and 1.975 (8) and 1.940 (8) Å for Ni(3), respectively. In a formal sense each OH group can therefore be considered to act as a five-electron donor ligand. The Ni–C and Ni–P bond lengths have normal values and compare well with similar distances reported in the literature for related complexes.[8]

The elucidation of the molecular structure of **3** by X-ray crystallography provides some clues on the formation of this complex from $NiCl_2(PMe_3)_2$ and Mg(R)Cl and allows one to design a rational preparative procedure for its high yield synthesis. Substantially improved, although still modest yields (ca. 30%) of **3** can reproducibly be obtained by reacting $NiCl_2(PMe_3)_2$ with 1.5 equiv of Mg(R)Cl and adding a drop of water after workup. This, together with the nature of **3**, suggests the participation in the reaction leading to its formation of the hydroxo complex **8** and of a reactive species able to generate the NiR_2 fragment, a suggestion which is also in agreement with the observation that **3** reacts with PMe_3 (eq 7) to yield the hydroxo com-

$$Ni_3R_4(PMe_3)_2(\mu\text{-}OH)_2 + 4PMe_3 \rightarrow [NiR(PMe_3)(\mu\text{-}OH)]_2 + Ni(PMe_3)_4 + R\text{–}R \quad (7)$$

plex **8** and $Ni(PMe_3)_4$ plus $C_{16}H_{18}$, i.e., the products re-

Scheme V. Possible Mechanism for the PMe_3-Catalyzed Synthesis of 3 from NiR_2(tmed) and the Dimeric Hydroxo Complex 8



sulting from the reductive elimination of $NiR_2(PMe_3)_2$ induced by PMe_3. In this way, it became clear that **3** could be obtained by the interaction of $[NiR(PMe_3)(\mu\text{-}OH)]_2$ with a NiR_2 generating complex. No reaction is however observed when **8** and $NiR_2(py)_2$ (**12**), or NiR_2(tmed) (**13**) are stirred at room temperature for several hours, but this is not completely unexpected in view of the stability of **12** and **13** toward dissociation of the N-containing ligand. The more labile $NiR_2(PMe_3)_2$ seems, in principle, a better choice, and indeed interaction of equimolar amounts of the hydroxo complex **8** with the dialkyl complex $NiR_2(PMe_3)_2$, generated in situ by addition of 2 equiv of PMe_3 to the tmed derivative **13**, provides complex **3**, although the reductive elimination products $Ni(PMe_3)_4$ and $C_{16}H_{18}$ are also obtained. The formation of the latter products is doubtless due to the action of the PMe_3 liberated in the course of the reaction leading to **3** on the still unreacted $NiR_2(PMe_3)_2$. To circumvent this difficulty, the dialkyl complex $NiR_2(PMe_3)_2$ was generated in small concentrations, although in a continuous and catalytic fashion, by the action of catalytic amounts of PMe_3 on the tmed complex **13**, as shown in Scheme V. Thus, stoichiometric amounts of complexes **8** and **13** provide very high yields (70–80%) of **3** when mixed in solutions which are 10^{-3}–10^{-4} M in PMe_3 (eq 8). This procedure seems to have general

$$[NiR(PMe_3)(\mu\text{-}OH)]_2 + NiR_2(tmed) \xrightarrow{[PMe_3]} Ni_3R_4(PMe_3)_2(\mu\text{-}OH)_2 + tmed \quad (8)$$

applicability. Work aimed at the synthesis of related trimetallic complexes of composition $Ni_3R_2R'_2(PMe_3)_2(\mu\text{-}OX)_2$, for various combinations of different alkyl groups R and R′ and X = H, Me, Et, ..., is presently under way.

Experimental Section

Microanalyses were by Pascher, Microanalytical Laboratory, Bonn. The spectroscopic instruments were Perkin-Elmer Models 577 and 684 for IR spectra and Perkin-Elmer R12 B and Varian XL-200 for NMR. The ^{13}C resonance of the solvent was used as internal standard, but chemical shifts are reported with respect to $SiMe_4$. ^{31}P NMR shifts are referenced to external 85% H_3PO_4. All preparations and other operations were carried out under oxygen-free nitrogen, following conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had a boiling point of 40–60 °C. $NaNC_4H_2\text{-}2,5\text{-}Me_2$ was prepared from NaH and 2,5-dimethylpyrrol. NaS_2CNMe_2 was dried by heating at 100 °C in vacuo for 7 days. PMe_3,[24] $NiCl_2(PMe_3)_2$,[10] and $Ni(cod)_2$[25] were prepared according to literature methods.

Preparation of $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)_2$ (1) and $Ni(\eta^3\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)$ (2). To a cold (−60 °C) suspension of $Ni(cod)_2$ (1.92 g, 7 mmol) in Et_2O (80 mL) were added PMe_3 (1.4 mL, 14 mmol) and $o\text{-}ClCH_2C_6H_4Me$ (0.92 mL, 7 mmol) via syringe, and the resulting mixture was stirred at room tem-

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perature for 7 h. After removal of the volatiles in vacuo, extraction with Et_2O (100 mL), and cooling at −30 °C, compound **1** was obtained as yellow-brown prisms in 90% yield. $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)_2$ (**1**): ^1H NMR (200 MHz, C_6D_6) δ 0.94 (br s, 18 H, PMe_3), 1.57 (s, 2 H, $CH_2C_6H_4Me$), 2.50 (s, 3 H, $CH_2C_6H_4Me$), 7.07 and 7.62 (m and d, 3 H and 1 H, respectively, $CH_2C_6H_4Me$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −15.5 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 5.1 (s, $CH_2C_6H_4Me$), 12.6 (br s, PMe_3), 21.3 (s, $CH_2C_6H_4Me$), 124.7, 125.3, 129.1, 131.9, 135.8, 146.9 (s, aromatics). Anal. Calcd for $C_{14}H_{27}P_2ClNi$: C, 47.8; H, 7.7. Found: C, 47.6; H, 7.8.

A similar procedure, using only 1 equiv of PMe_3, afforded **2** as red plates in 70% yield. $Ni(\eta^3\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)$ (**2**): ^1H NMR (200 MHz, C_6D_6) δ 0.90 (br d, 9 H, $^2J_{HP}$ = 8 Hz, PMe_3), 1.09 (br s, 2 H, $CH_2C_6H_4Me$), 1.97 (s, 3 H, $CH_2C_6H_4Me$), 7.0–7.3 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −6.6 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 15.2 (d, $^1J_{CP}$ = 29 Hz, PMe_3), 19.9 (s, $CH_2C_6H_4Me$), 20.6 (br s, $CH_2C_6H_4Me$), 107.9 and 114.7 (br s, aromatics bound to Ni), 128.0, 132.4, 132.7, 134.6 (s, aromatics). Molecular weight (cryoscopically in C_6H_6, N_2) Calcd for $C_{11}H_{18}PClNi$: 275. Found: 274. Anal. Calcd for $C_{11}H_{18}PClNi$: C, 47.9; H, 6.5. Found: C, 47.7; H, 6.5.

Interconversion Reactions of 1 and 2. (a) A suspension of $Ni(\eta^3\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)$ (**2**) (0.31 g, 1.1 mmol) in Et_2O (20 mL) was treated with PMe_3 (0.12 mL, 1.2 mmol). The red starting material dissolved immediately, and the color of the solution changed to yellow. After 3 h of stirring at room temperature the solvent was evaporated to dryness and the residue crystallized from Et_2O at −20 °C to afford yellow crystals of **1** in 45% yield.

(b) $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)_2$ (**1**) (0.09 g, 0.2 mmol) and $Ni(cod)_2$ (0.02 g, 0.06 mmol) were treated with 15 mL of Et_2O, and the mixture was stirred for 5 h. The dark red solution that resulted was then evaporated under vacuum and crystallized from Et_2O, at −20 °C, to provide red crystalline **2** in 30% yield.

Reactivity of $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)_2$ (1). (a) With Carbon Monoxide. CO was bubbled (20 °C, 1 atm) through a solution of **1** (0.35 g, 1 mmol) in Et_2O (30 mL). The reaction, almost instantaneously, precipitated an orange microcrystalline solid. The volatiles were removed in vacuo, and the residue was dissolved in diethyl ether. The acyl derivative **4** was obtained in almost quantitative yield by filtration, partial removal of the solvent, and cooling at −30 °C. A microanalytical sample was obtained, in the form of orange crystals, by cooling a saturated solution at 0 °C. $Ni(COCH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)_2$ (**4**): ^1H NMR (200 MHz, C_6D_6) δ 0.90 (br s, 18 H, PMe_3), 2.61 (s, 3 H, $CH_2C_6H_4Me$), 3.89 (s, 2 H, $COCH_2C_6H_4Me$), 6.98 and 7.60 (m and d, 3 H and 1 H, respectively, $CH_2C_6H_4Me$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −15.4 s; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 13.2 (br s, PMe_3), 20.8 (s, $CH_2C_6H_4Me$), 56.5 (s, $COCH_2C_6H_4Me$), 126.2, 126.7, 130.5, 130.8 (s, aromatic C–H carbons), 133.3, 136.7 (s, aromatic quaternary carbons), 253.0 (br s, COR); IR (Nujol mull) ν(C=O) 1610 cm^{-1}. Anal. Calcd for $C_{15}H_{27}OP_2ClNi$: C, 47.5; H, 7.1. Found: C, 47.9; H, 7.2.

(b) With KSCN. A mixture of $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)_2$, (**1**) (0.43 g, 1.2 mmol) and powdery KSCN (an excess) was stirred in acetone (30 mL) for 2 h. Evaporation of the solvent, extraction with Et_2O, and centrifugation furnished a clean solution from which complex **5** was obtained in 90% yield by removal of the solvent and cooling at −30 °C. $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)(NCS)(PMe_3)_2$ (**5**): ^1H NMR (200 MHz, C_6D_6) δ 0.77 (br s, 18 H, PMe_3), 1.24 (s, 2 H, $CH_2C_6H_4Me$), 2.33 (s, 3 H, $CH_2C_6H_4Me$), 7.01 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −11.8 (br s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 5.8 (s, $CH_2C_6H_4Me$), 12.9 (br s, PMe_3), 21.2 (s, $CH_2C_6H_4Me$), 124.8, 125.4, 129.2, 131.7 (s, aromatic CH carbons), 135.7, 146.6 (aromatic quaternary carbons); IR (Nujol mull) ν(NCS) 2100 cm^{-1}.

(c) With $NaNC_4H_2Me_2$. One equivalent of sodium 2,5-dimethylpyrrolyl (16.5 mL of a 0.3 M solution prepared from $HNC_4H_2Me_2$ and NaH in THF) was added to a cold stirred solution of **1** (1.74 g, 4.9 mmol) in Et_2O (80 mL). After the solution was stirred for 5 h at room temperature, the volatiles were removed under vacuum. Crystallization of the residue from Et_2O at −20 °C afforded orange prisms of complex **6** in 35% yield. In addition, orange crystals of the hydroxo species **8** (see text) can also be obtained from the reaction mixture. $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)(\eta^1\text{-}NC_4H_2Me_2)(PMe_3)_2$ (**6**): ^1H NMR (60 MHz, C_6H_6) δ 0.81 (pt, 18 H, PMe_3, J_{HPapp} = 3.4 Hz), 1.42 (t, 2 H, Ni–CH_2, $^3J_{HP}$ = 10 Hz), 2.59 (s, 3 H, $CH_2C_6H_4Me$), 2.92 (s, 6 H, $NC_4H_2Me_2$). Anal. Calcd for $C_{20}H_{35}NP_2Ni$: C, 58.6; H, 8.5. Found: C, 58.3; H, 8.7. Compound **6** decomposes readily in the presence of water to give the dimeric hydroxo species **8**.

(d) With an Excess of PMe_3. A solution of **1** (0.30 g, 0.8 mmol) in Et_2O (20 mL) was treated with 0.4 mL of neat PMe_3. The mixture was stirred at room temperature for 2–3 h and then cooled at −30 °C. Crystalline dark blue $NiCl_2(PMe_3)_2$ (0.10 g, 0.3 mmol) was filtered off and the mother liquor taken to dryness. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ studies, carried out with a C_6D_6 solution of the residue, reveal the presence of $Ni(PMe_3)_4$ and $C_{16}H_{18}$ (1,2-bis(2-methylphenyl)ethane identified by comparison of its IR, ^1H, and ^{13}C NMR spectra with those of an authentic sample) as the major species in solution.

Reactivity of $Ni(\eta^3\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)$ (2). (a) With KI. A solution of **2** (0.37 g, 1.3 mmol) in a 2:1 mixture of Et_2O–acetone (45 mL) was treated with an excess of KI. The reaction mixture darkened considerably, and after 2 h of stirring the solvent was removed under reduced pressure. Extraction with Et_2O, centrifugation, and cooling at −30 °C furnished green-red prisms (green by reflected light, red by transmitted light) of the desired complex **7**, which were washed with petroleum ether and dried in vacuo; yield 90%. $Ni(\eta^3\text{-}CH_2C_6H_4\text{-}o\text{-}Me)I(PMe_3)$ (**7**): ^1H NMR (200 MHz, C_6D_6) δ 1.02 (br d, 9 H, PMe_3, $^2J_{HP}$ = 10 Hz), 1.30 (br s, 2 H, $CH_2C_6H_4Me$), 1.94 (s, 3 H, $CH_2C_6H_4Me$), 6.15 and 7.20 (multiplets, aromatics); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −2.9 (br s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 17.4 (d, PMe_3, $^1J_{CP}$ = 30 Hz), 19.9 (s, $CH_2C_6H_4Me$), 28.2 (s, $CH_2C_6H_4Me$), 108.6 and 113.5 (s, aromatics, C–H and quaternary respectively, bound to Ni), 132.2, 133.7, 135.8 (s, aromatics). Molecular weight (cryoscopically in C_6H_6, N_2) Calcd for $C_{11}H_{18}PINi$: 366. Found: 364.

(b) With Potassium Hydroxide. Following a similar procedure to that described above for the KI reaction, but with use of finely divided KOH, orange crystals of the dimeric hydroxo complex could be isolated in 85% yield. $[Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2$ (**8**): ^1H NMR (200 MHz, C_6D_6) δ −4.77 (s, 1 H, μ-OH), 0.43 (d, 9 H, PMe_3, $^2J_{PH}$ = 8.0 Hz), 0.95 (d, 2 H, $CH_2C_6H_4Me$, $^3J_{HP}$ = 9.9 Hz), 2.88 (s, 3 H, $CH_2C_6H_4Me$), 6.95–7.21 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −8.4 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 4.7 (d, $CH_2C_6H_4Me$, $^2J_{CP}$ = 28.0 Hz), 11.8 (d, PMe_3, $^1J_{CP}$ = 28.2 Hz), 21.6 (s, $CH_2C_6H_4Me$), 122.1, 125.6, 130.0 (s, CH aromatics), 134.5 and 150.9 (s, quaternary aromatics); IR (Nujol mull) ν(OH) 3590 cm^{-1}. Molecular weight (cryoscopically in C_6H_6, N_2) Calcd for $C_{22}H_{38}O_2P_2Ni_2$: 513.4. Found: 461. Anal. Calcd for $C_{22}H_{38}O_2P_2Ni_2$: C, 51.4; H, 7.4. Found: C, 51.5; H, 7.4.

When complex **8** is crystallized from Et_2O or petroleum ether in the presence of 2,5-dimethylpyrrole red brown crystals of the adducts $\mathbf{8}\cdot HNC_4H_2Me_2$ and $\mathbf{8}\cdot 2HNC_4H_2Me_2$ can be obtained in good yields. NMR studies show these adducts are completely dissociated in benzene solutions. In the absence of added 2,5-dimethylpyrrole recrystallization of these materials from Et_2O affords the base-free parent complex **8**. $[Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2\cdot HNC_4H_2Me_2$: IR (Nujol mull) ν(OH) 3580 cm^{-1}, ν(NH) 3260 (br), 3200 (br) cm^{-1}. Anal. Calcd for $C_{28}H_{47}O_2NP_2Ni_2$: C, 55.2; H, 7.7. Found: C, 55.2; H, 7.8. $[Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2\cdot 2HNC_4H_2Me_2$: IR (Nujol mull) ν(OH) 3570 cm^{-1}, ν(NH) 3200 (br), 3140 (br) cm^{-1}. Anal. Calcd for $C_{34}H_{56}O_2N_2P_2Ni_2$: C, 58.0; H, 8.0; N, 4.0. Found: C, 57.3; H, 7.9; N, 4.1.

(c) With NaCp. $Ni(\eta^3\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)$ (**2**) (0.22 g, 0.8 mmol) was dissolved in Et_2O (40 mL) and the resulting red solution cooled at −40 °C and reacted with 1 equiv of NaCp (1 mL of a 0.8 N solution in THF) added via syringe. The mixture was stirred for 4 h at room temperature and taken to dryness and the residue extracted with 30 mL of Et_2O. Green crystals were obtained in 75% yield by partial removal of the solvent and cooling at −30 °C. Further purification can be achieved by recrystallization from Et_2O–petroleum ether (1:1) at −30 °C. $Ni(\eta^5\text{-}C_5H_5)(\eta^1\text{-}CH_2C_6H_4Me)(PMe_3)$ (**9**): ^1H NMR (200 MHz, C_6D_6) δ 0.70 (d, 9 H, PMe_3, $^2J_{HP}$ = 8.5 Hz), 1.59 (d, 2 H, $CH_2C_6H_4Me$, $^3J_{HP}$ = 9 Hz), 2.41 (s, 3 H, $CH_2C_6H_4Me$), 4.80 (s, 5 H, C_5H_5), 7.27 and 7.07 (m, 4 H, $CH_2C_6H_4Me$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −3.09 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ −2.4 (d, $CH_2C_6H_4Me$, $^2J_{CP}$ = 21 Hz), 17.0 (d, PMe_3, $^1J_{CP}$ = 28 Hz), 20.7 (s, $CH_2C_6H_4Me$), 91.1 (s, C_5H_5), 122.0, 125.7, 127.3, 129.8 (s, phenylic CH carbons), 133.0 and 155.1 (s, quaternary phenylic carbons). Anal. Calcd for $C_{16}H_{23}PNi$: C, 63.0;

H, 7.5. Found: C, 63.3; H, 6.2.

(d) With Sodium Dialkyldithiocarbamates. An excess of dried, finely ground NaS_2CNR_2 (R = Me, *i*-Pr) was added as a solid to a stirred solution of $Ni(\eta^3\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)$ (**2**) (0.16 g, 0.6 mmol) in acetone (20 mL). An instantaneous reaction occurred accompanied by a change in the color of the solution from the starting red-purple to orange-red. The complexes were obtained as dark red needles from Et_2O at 0 °C (R = Me) or ochre octahedra from Et_2O at −30 °C (R = *i*-Pr). $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)(S_2CNMe_2)(PMe_3)$ (**10**): ^1H NMR (200 MHz, C_6D_6) δ 0.76 (d, 9 H, PMe_3, $^2J_{HP}$ = 8.5 Hz), 1.77 (s, 2 H, $CH_2C_6H_4Me$), 2.29 (s, 6 H, S_2CNMe_2), 2.61 (s, 3 H, $CH_2C_6H_4Me$), 7.06–7.20 (m, 4 H, $CH_2C_6H_4Me$); IR (Nujol mull) ν(C=N) 1530 cm^{-1}. Anal. Calcd for $C_{14}H_{24}NS_2PNi$: C, 46.7; H, 6.7. Found: C, 46.4; H, 6.8. $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)(S_2CN\text{-}i\text{-}Pr_2)(PMe_3)$ (**11**): ^1H NMR (200 MHz, C_6D_6, 70 °C) δ 0.88 (d, 9 H, PMe_3, $^2J_{HP}$ = 8.5 Hz), 0.97 (d, 12 H, $S_2CN(CHMe_2)_2$, $^3J_{HH}$ = 6.6 Hz), 1.81 (s, 2 H, $CH_2C_6H_4Me$), 2.60 (s, 3 H, $CH_2C_6H_4Me$), 4.30 (br m, 2 H, $S_2CN(CHMe_2)_2$), 7.00–7.60 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C) δ −8.2 (s); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) δ 12.6 (d, PMe_3, $^1J_{CP}$ = 26 Hz), 12.6 (s, $CH_2C_6H_4Me$), 19.3 (br s, $S_2CN(CHMe_2)_2$), 21.8 (s, $CH_2C_6H_4Me$), 50.1 (br s, $S_2CN(CHMe_2)_2$), 122.0, 125.4, 128.1, 129.6 (s, aromatic CH carbons), 133.8, 151.6 (s, quaternary aromatic carbons), 208.9 (s, S_2CNR_2). IR (Nujol mull) ν(C=N) at 1470 cm^{-1}.

Bis(*o*-xylyl) Complexes. (a) $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)_2(NC_5H_5)_2$ (12). A stirred suspension of $NiCl_2(py)_4$ (1.34 g, 3 mmol) in Et_2O (40 mL) at −60 °C was treated with pyridine (2 mL) and $Mg(CH_2C_6H_4\text{-}o\text{-}Me)Cl$ (12 mL of a 0.5 M diethyl ether solution). The resulting mixture was stirred at room temperature for 30 min, the solvent removed under reduced pressure and the residue extracted with petroleum ether (80 mL); centrifugation, concentration of the resulting solution, and cooling at −30 °C overnight furnished the product as dark red prisms. The high solubility of this compound is probably responsible for the low yield of crystalline material, 20–30% yield. This complex is best stored in sealed ampules under vacuum. $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)_2(py)_2$ (**12**): ^1H NMR (200 MHz, C_6D_6) δ 2.14 (s, 4 H, $CH_2C_6H_4Me$), 2.40 (s, 6 H, $CH_2C_6H_4Me$), 6.30–6.95 and 8.02 (4 m, 18, H, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 18.8 (s, $CH_2C_6H_4Me$), 21.2 (s, $CH_2C_6H_4Me$), 118.9, 120.9, 126.3, 129.4 (s, CH phenyl carbons), 123.3, 134.3, 149.3 (s, the first being somewhat broad, CH pyridine carbons), 133.3 and 143.9 (s, quaternary phenyl carbons). Anal. Calcd for $C_{26}H_{28}N_2Ni$: C, 73.8; H, 5.7. Found: C, 71.8; H, 6.6.

(b) $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)_2(tmed)$ (13). A concentrated petroleum ether solution of the bis(pyridine) complex, obtained as indicated above, was cooled at −60 °C and reacted with an excess of tmed. The brick red microcrystalline solid that precipitated was filtered off and dried under vacuum (yield 20%). Although this material is pure enough for most purposes, it may be recrystallized from cold petroleum ether to afford analytical samples in the form of dark red prisms. $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)_2(tmed)$ (**13**): ^1H NMR (200 MHz, C_6D_6) δ 1.01 and 1.24 (s, 4 H and 4 H, $CH_2C_6H_4Me$ and NCH_2CH_2N; the assignment may be reversed), 1.69 (s, 12 H, *Me*N), 2.85 (s, 6 H, $CH_2C_6H_4Me$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 8.9 (s, $CH_2C_6H_4Me$), 22.2 (s, $CH_2C_6H_4Me$), 46.8 (s, *Me*N), 58.8 (s, NCH_2CH_2N), 121.5, 124.7, 129.0, 130.1 (s, aromatic CH carbons), 135.1, 154.3 (s, aromatic quaternary carbons). Anal. Calcd for $C_{22}H_{34}N_2Ni$: C, 68.6; H, 8.8. Found: C, 67.8; H, 8.7.

Attempted Preparation of $Ni(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)_2(PMe_3)_2$. (a) $NiCl_2(PMe_3)_2$ + 2 $Mg(CH_2C_6H_4\text{-}o\text{-}Me)Cl$. The bis(*o*-methylbenzyl) complex $Ni(\eta^1\text{-}CH_2C_6H_4Me)_2(PMe_3)_2$ could not be obtained by reaction of the dichloride with 2 equiv of the Grignard reagent. The only nickel-containing compounds isolated from this reaction were complexes **1**, **2**, and **3**.

(b) $Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2(py)_2$ + PMe_3. This alternative route is also unsuccessful for the synthesis of $Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2(PMe_3)_2$. When the pyridine complex is reacted at −60 °C with an excess of PMe_3, the only products detected are $Ni(PMe_3)_4$ and $C_{16}H_{18}$ (1,2-bis(2-methylphenyl)ethane). The use of 2 equiv of PMe_3 affords also the reductive elimination products $Ni(PMe_3)_4$ and $C_{16}H_{18}$, together with minor amounts of complex **3**.

Synthesis of $Ni_3(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)_4(PMe_3)_2(\mu_3\text{-}OH)_2$ (3). (a) $NiCl_2(PMe_3)_2$ (0.28 g, 1 mmol), stirred in 30 mL of Et_2O, at −40 °C, was treated with 3 mL of a 0.5 M solution of $Mg(CH_2C_6H_4\text{-}o\text{-}Me)Cl$, and the mixture was allowed to warm up to room temperature and stirred for 4 h. The solvent was removed in vacuo, and the residue was extracted with 40 mL of petroleum ether. After centrifugation, concentration of the solution to 5 mL, addition of a drop of water, and cooling at −20 °C for 48 h, complex **3** was obtained in 30% yield.

(b) A mixture of the hydroxo complex **8** (0.32 g, 0.62 mmol) and a slight excess of the tmed complex **13** (0.3 g, 0.75 mmol) were stirred in 30 mL of Et_2O at room temperature. The sparingly Et_2O-soluble hydroxo complex remains undissolved under these conditions, but it dissolves immediately upon addition of small amounts of PMe_3 (0.2 mL of a 0.1 M solution, 0.02 mmol) with concomitant precipitation of a dark red, nearly black, microcrystalline solid. After the mixture was stirred at room temperature for 2 h and cooled at −30 °C for 30 min, 0.34 g of **3** was collected (70% yield). $Ni_3(\eta^1CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)_2(\mu_3\text{-}OH)_2$ (**3**): IR (Nujol mull) ν(OH) 3570 cm^{-1}. Anal. Calcd for $C_{38}H_{56}P_2O_2Ni_3$: C, 58.3; H, 7.2; O, 4.1. Found: C, 57.7; H, 7.1; O, 4.8.

Crystallographic Studies. The air-sensitive crystals of **2** and **3** were mounted in glass capillaries under N_2 atmosphere and mounted on the goniometer head. Data were collected and reduced, and a set of 1476 unique reflections (compound **2**) and 1983 reflections (compound **3**) were used in subsequent calculations. The analysis of the Patterson map of each compound permitted the location of the Ni, Cl, and P atoms (compound **2**) and of the three independent Ni atoms (compound **3**). The rest of the non-hydrogen atoms were soon located after several cycles of Fourier synthesis. The H atoms were geometrically placed, except those corresponding to the OH groups in **3**. None of them were refined. The anisotropic refinement of the non-hydrogen atoms converged smoothly at R = 0.053 (compound **2**) and 0.044 (compound **3**). A summary of crystal data is given in Table I. All computations were made with the Oxford CRYSTALS package.[26] The atomic scattering factors were taken from Cromer and Mann.[27] In the last stages of the refinement of complex **3**, each reflection was given a weight computed from a Chebyshev series, with three coefficients: 30.3, 45.4, and 7.5. Unit weights were used for complex **2**.

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Registry No. **1**, 98170-36-6; **2**, 108694-94-6; **3**, 98170-38-8; **4**, 98170-39-9; **5**, 108741-30-6; **6**, 108741-31-7; **7**, 108710-78-7; **8**, 108694-95-7; **8**.$HNC_4H_2Me_2$, 108694-98-0; **8**.$2HNC_4H_2Me_2$, 108710-79-8; **9**, 98170-44-6; **10**, 98170-45-7; **11**, 98170-46-8; **12**, 108694-96-8; **13**, 108694-97-9; $Ni(cod)_2$, 1295-35-8; *o*-$ClCH_2C_6H_4Me$, 552-45-4; $NiCl_2(PMe_3)_2$, 19232-05-4; $Ni(PMe_3)_4$, 28069-69-4; $C_{16}H_{18}$, 952-80-7; NaS_2CNMe_2, 128-04-1; $NaS_2CN(i\text{-}Pr)_2$, 4092-82-4; $NiCl_2(Py)_4$, 14076-99-4; $Mg(CH_2C_6H_4\text{-}o\text{-}Me)Cl$, 29875-05-6; Ni, 7440-02-0.

Supplementary Material Available: Tables of thermal parameters for **2** and **3** (3 pages); listings of observed and calculated structure factors for **2** and **3** (36 pages). Ordering information is given in any current masthead page.

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