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Thermal Dimerization of 1-Phenyl-3,4-dimethylphosphole. An Access to 2,2′-Biphospholenes and Complexes Thereof

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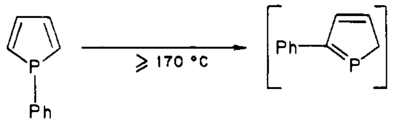
Thermolysis of 1-phenyl-3,4-dimethylphosphole in alcoholic solvents between 140 and 170 °C in the presence of anhydrous nickel(II) chloride leads to the synthesis of racemic dichloro[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II), $LNiCl_2$, in reasonable yield. This reaction represents the first synthesis of a biphospholene and occurs with remarkable stereoselectivity. None of the meso diastereomer is detected in this reaction. This new complex has been characterized by elemental analyses, ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^1H\{^{31}P\}$, and $^{13}C\{^1H, ^{31}P\}$ NMR spectroscopy, mass and infrared spectroscopy, cyclic voltammetry, and X-ray crystallography. The molecule crystallizes in the monoclinic space group $C2/c$ in a unit cell of dimensions $a = 14.127$ (5) Å, $b = 9.611$ (3) Å, $c = 17.777$ (6) Å, $\beta = 106.81$ (2)°, $\rho_{calcd} = 1.455$ g cm^{-3}, and $\rho_{obsd} = 1.43 \pm 0.02$ g cm^{-3}, with $Z = 4$. Refinement converged to $R = 0.041$ with 1486 independent reflections. The nickel atom deviates from square planarity only slightly, and both the Ni–Cl (2.201 Å) and Ni–P (2.126 Å) bonds are short. The chelate ring is rigid and contains four stereocenters. The ligand has been liberated from nickel by cyanide displacement in a two-phase solvent system (CH_2Cl_2/H_2O) and converted to its dioxide and disulfide. It has also been transferred to ruthenium to form *trans*-L_2RuCl_2, to platinum to form $LPtCl_2$ and to palladium without epimerization to form $LPdCl_2$. All these new compounds have been fully characterized by the above techniques, including X-ray crystallography for $LPdCl_2$. This molecule crystallizes in the monoclinic space group $P2_1/n$ in a unit cell of dimensions $a = 15.199$ (3) Å, $b = 17.844$ (4) Å, $c = 8.900$ (2) Å, $\beta = 90.97$ (2)°, $V = 2413$ Å^3, $\rho_{calcd} = 1.518$ g cm^{-3}, and $\rho_{obsd} = 1.49 \pm 0.02$ g cm^{-3}, with $Z = 4$. Refinement converged to $R = 0.056$ with 2840 independent reflections. The palladium atom deviates from square planarity by a smaller amount than does the nickel atom in the nickel complex, and the Pd–Cl (2.366 Å) and Pd–P (2.218 Å) bonds are long and short, respectively, suggesting that the biphospholene is a good donor. A mechanism for the formation of $LiNiCl_2$ is presented.

Introduction

In continuation of our studies of the coordination chemistry of phospholes[2] and their novel reactions,[3-6] we have investigated the thermolysis of 1-phenyl-3,4-dimethylphosphole in the presence of anhydrous nickel(II) chloride. We have previously shown[5] that 1-phenylphospholes rearrange at high temperature through 1,5-phenyl migrations to give 2*H*-phospholes (reaction 1), and it has been possible to trap one such 2*H*-phosphole by reaction with $[(\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ (reaction 2).



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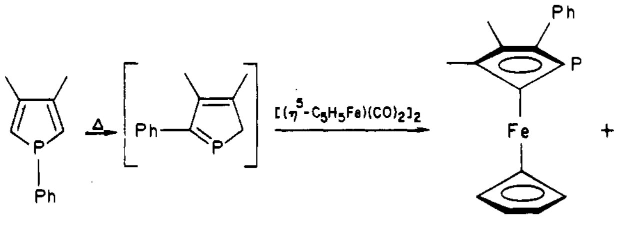
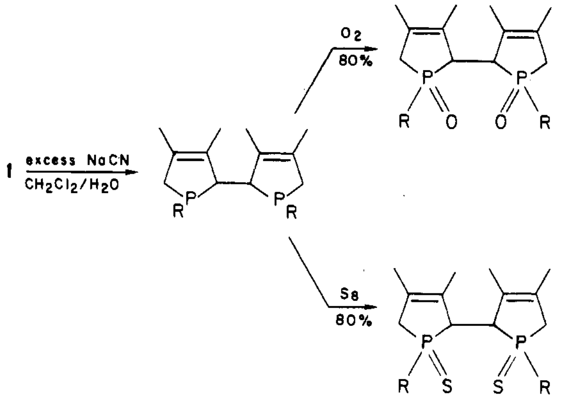
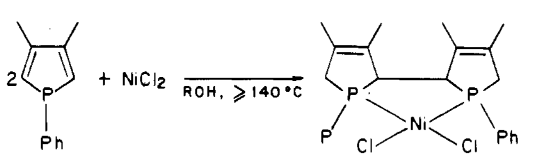


other products (2)

Thus, we hoped that at high temperatures the reactions of 1-phenylphospholes with metal halides would lead to new types of complexes instead of the classical complexes[2] obtained under standard conditions. Indeed, we observed that thermolysis of 1-phenyl-3,4-dimethylphosphole with nickel(II) chloride in an alcohol solvent at temperatures between 140 and 170 °C produced an entirely new ligand complex,[7] **1**, according to reaction 3. We report herein the details of this reaction, studies directed at discerning its mechanism, and transfer of the ligand to other metals.

Scheme I





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Results and Discussion

Thermolysis in alcoholic solvents at temperatures between 140 and 170 °C of 1-substituted 3,4-dimethylphospholes in the presence of anhydrous nickel(II) chloride leads to the synthesis of [2,2′-bi(1-R-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II) (**1**) in 30% yield, R = Ph, *t*-Bu. The ligand may be liberated from nickel by using sodium cyanide in a two-phase (CH_2Cl_2/H_2O) system under argon or nitrogen and converted into its dioxide and disulfide with oxygen and sulfur, respectively (see Scheme I). Due

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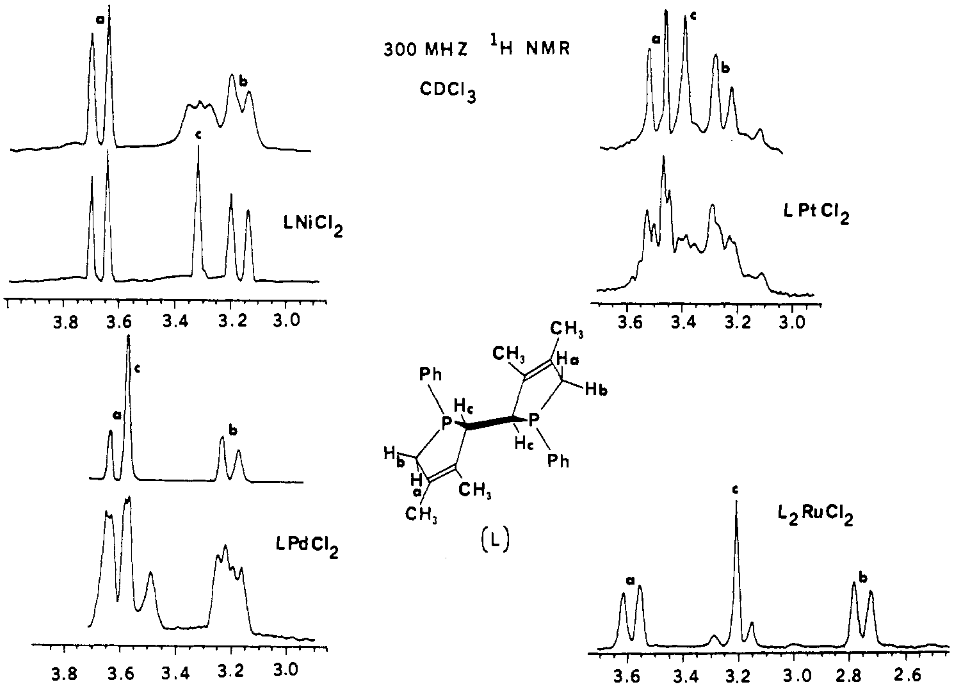
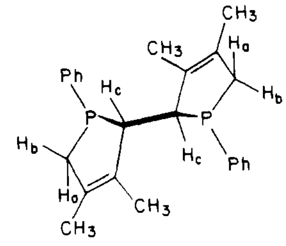


Figure 1. 300-MHz ^{1}H NMR spectra in the 3.0–3.8 ppm region in CDCl$_3$ at 30 °C. The lower trace of each pair except for LNiCl$_2$ is the conventional spectrum, and the upper trace is the phosphorus-decoupled spectrum. For the complex L$_2$RuCl$_2$, only one spectrum is shown as it is identical with and without phosphorus decoupling.

to their extreme air sensitivity, the ligands themselves have not been isolated in pure form but only characterized in situ by ^{31}P NMR spectroscopy ($\delta(^{31}P) = -28.3, -5.39$; R = Ph, *t*-Bu, respectively). The ^{31}P chemical shifts of these two biphospholenes are in the same relative position as those of the starting phospholes ($\delta(^{31}P) = -2.5, 27.5$; R = Ph, *t*-Bu, respectively) and downfield of that for analogous phospholenes[8] (cf. $\delta(^{31}P) = -34.5$ for 1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole).

The ligands may be transferred from nickel to other metals in high yield by the same cyanide displacement technique. Thus, reactions of a CH$_2$Cl$_2$ solution of the liberated biphospholene, L, with (PhCN)$_2$PdCl$_2$, (CH$_3$CN)$_2$PtCl$_2$, and (Ph$_3$P)$_3$RuCl$_2$ produce LPdCl$_2$, LPtCl$_2$, and *trans*-L$_2$RuCl$_2$, respectively. These complexes are all nonelectrolytes and exhibit ν_{MCl}, the metal chloride vibrations, in the expected region[9-11] (ν_{NiCl} 317, 341 cm^{-1}; ν_{PdCl} 277, 302 cm^{-1}; ν_{RuCl} 322 cm^{-1}; ν_{PtCl} 286, 306 cm^{-1}). The ^{31}P NMR spectra of these compounds show singlets in each case (Table I) and do not permit us to conclude whether they exist as mixtures of diasteromers or as a single diastereomer.[12] It is well-known that the phosphorus atoms contained in five-membered chelate rings exhibit an anomalously large coordination chemical shift, $\Delta\delta$, which can be considered as being made up of the expected coordination chemical shift (calculated from the relation[13] $\Delta\delta = A\delta(\text{ligand}) + B$) together with a ring contribution,[14] ΔR, i.e., $\Delta\delta_{obsd} = \Delta\delta + \Delta R$. If we assume values of ΔR similar to those recently reported for other unsymmetrical bidentate phosphines[9] (ΔR = 42, 33, 29 ppm for Ni, Pd, and Pt complexes, respectively), we then calculate $\Delta\delta$ to be 38, 53, and 24 ppm for the Ni, Pd, and Pt biphospholene complexes. These values in addition to the actual $\Delta\delta_{obsd}$ values are larger than those observed[9,12] for other unsymmetrical bidentate phosphines, suggesting that this biphospholene ligand is a very good donor.

The synthesis of the nickel complex produces exclusively a racemic mixture of a single diastereomer as shown by X-ray crystallography (vide infra) despite the possibility with the presence of 4 stereocenters[15] of forming 16 diastereomers. The ^{1}H NMR spectra of these new compounds, all of which possess the ligand conformation **2**, are second order, and the assignments were made



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by a combination of field-dependence studies (80, 100, 200, 300 MHz), phosphorus decoupling, and noting of the effect of the metal. In addition, the ^{1}H NMR spectrum of the ruthenium complex provided very useful information. This complex exists as a racemic mixture of two diastereomers; the *R,R;R,R* and *S,S;S,S* forms. This is because steric encumbrances preclude formation of the *R,R;S,S* (meso) diastereomer. Molecular models demonstrate that for this complex H$_b$ (see **2** above) is situated near the shielding region of an adjacent phenyl ring while H$_a$ is situated near the deshielding region of the same phenyl ring. This coupled with the observation that ^{31}P decoupling does not change the ^{1}H NMR spectrum in the 2.6–3.6 ppm region (Figure 1) for this compound, allows assignment of the chemical shifts of the ring methylene and methine protons. H$_a$ and H$_b$ occur as an AB quartet (either J_{PH_a} and J_{PH_b} or $|^2J_{PH_a} + {}^4J_{PH_a}|$ and $|^2J_{PH_b} + {}^4J_{PH_b}|$ are zero[16]) with $\delta_A = 3.58$, $\delta_B = 2.75$, $J_{AB} = 17.5$ Hz, and H$_c$ as a singlet at δ 3.18. The assignment of this spectrum then allowed similar assignments to be made for the other compounds (Table I). These assignments are consistent with those previously made for phospholene oxides,[17] where it was observed that $^2J_{PH}$ ranges

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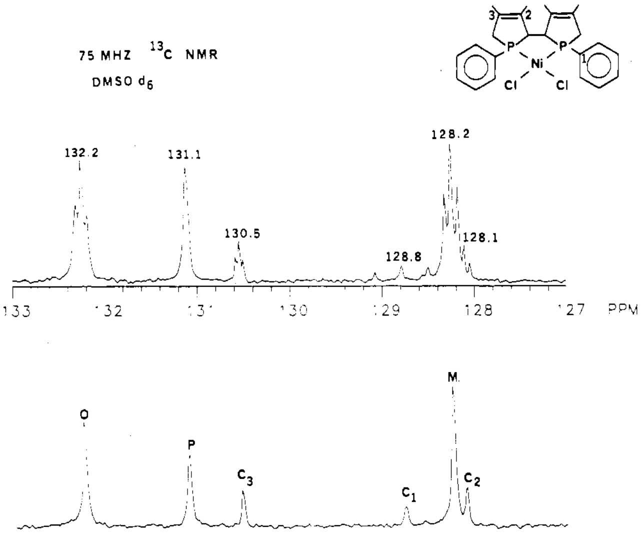

Figure 2. 75-MHz $^{13}C\{^1H\}$ (upper) and $^{13}C\{^1H,^{31}P\}$ NMR (lower) spectra in the aromatic region for $LNiCl_2$ in Me_2SO-d_6 at 30 °C.

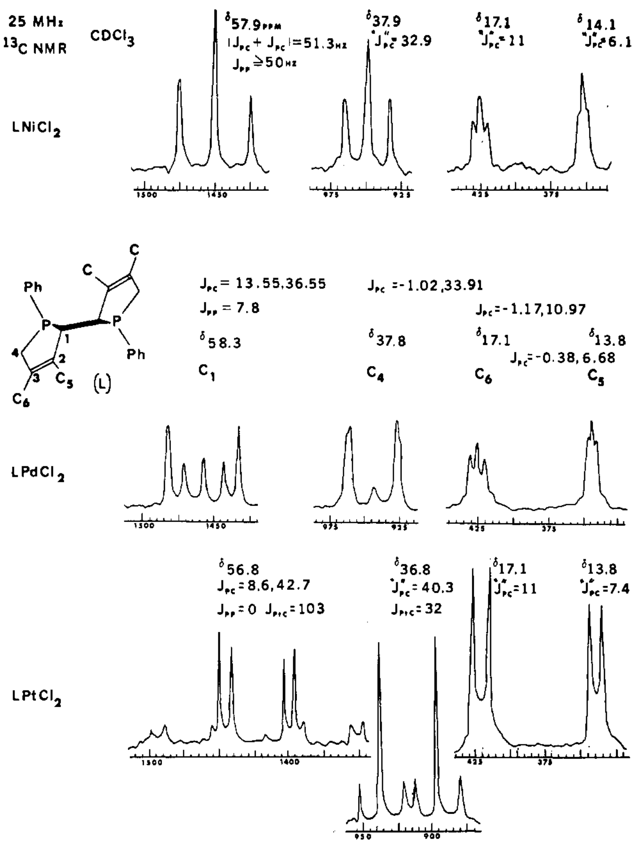

Figure 3. 25-MHz $^{13}C\{^1H\}$ NMR spectra in the aliphatic region for $LNiCl_2$, $LPdCl_2$, and $LPtCl_2$. These spectra illustrate the various line shapes possible for the AXX′ spin system. In these cases, the major change is in $^2J_{PP}$ while the $|^nJ_{PC} + {}^{n+2}J_{PC}|$ values remain relatively constant.

from 9 to 16 Hz depending upon the geometric interrelationship of the hydrogens and the P=O bond. Thus, it appears logical that $^2J_{PH}$ and $^4J_{PH}$ are not zero for the ruthenium complex but rather that they have equal magnitudes but opposite signs.[16] The PH coupling constants were not determined for the other compounds, but as Figure 1 shows, they are not zero.

The $^{13}C\{^1H\}$ NMR spectra of these compounds displayed AXX′ multiplets,[18] A ≡ ^{13}C, X ≡ ^{31}P, for each carbon resonance and

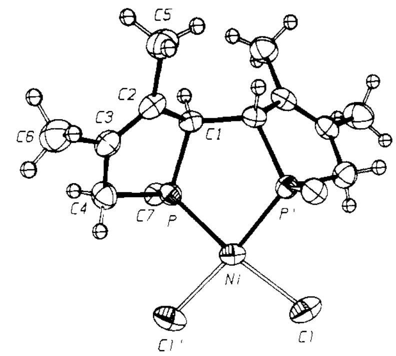

Figure 4. ORTEP plot of the structure of $LNiCl_2$ showing the atom-labeling scheme (50% probability ellipsoids, except for hydrogens at 10%). Phenyl groups have been omitted for clarity.

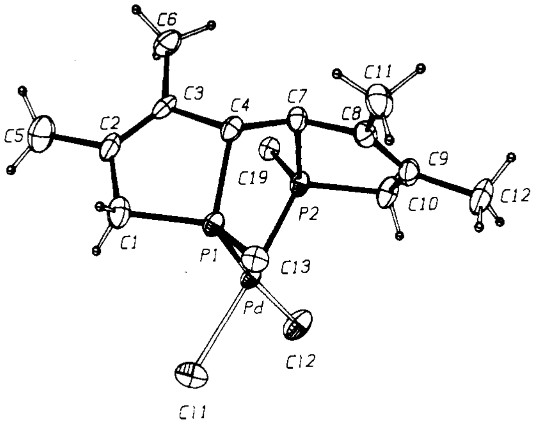

Figure 5. ORTEP plot of the structure of $LPdCl_2$ showing the atom-labeling scheme (50% probability ellipsoids, except for hydrogens at 10%). Phenyl groups have been omitted for clarity.

presented some ambiguity in assignment. In order to facilitate assignment, particularly of the resonances due to carbons 2 and 3 and the phenyl ipso carbon, a $^{13}C\{^1H,^{31}P\}$ spectrum was obtained (Figure 2). This spectrum together with the spectrum of the complex (**1**, R = *t*-Bu) allowed complete assignment of all resonances (Table II). The upfield shift due to steric compression[17,19] was used to differentiate the resonances due to carbons 2 from 3 and 5 from 6 with the former of each pair anticipated to resonate upfield of the latter. Five-line multiplets were observed (Figure 3) for some of the resonances, allowing determination of $^2J_{PP}$, and it was found to decrease in the order Ni > Pd > Pt as expected.[9] The spin system for the ruthenium complex is $A[X]_4$, and the coupling constants given for this compound in Table II are for the separations equivalent to the $A[X]_2$ spin system for comparison with the other data. The combined NMR spectrscopic data suggest that the ligand has the same conformation in each of these complexes.

In order to gain more conclusive support for this conclusion and to better characterize this new ligand system, X-ray crystal structures of $LNiCl_2$ (**1**) and $LPdCl_2$ (**3**) were obtained. ORTEP diagrams of complexes **1** and **3** are shown in Figures 4 and 5, respectively. Both complexes exist as discrete molecular entities with no abnormal intermolecular contacts. Each complex contains a C_2 axis passing through the metal atom bisecting the Cl–M–Cl angle as the only element of molecular symmetry. As a result, both complexes are chiral. The fractional atomic coordinates are given in Tables III and IV, and important bond distances and angles are given in Tables V and VI. As can be seen in Figures 4 and 5, the conformation of the chelate ring is rigid with the two phenyl rings so disposed as to create a cleft approximately normal to a line joining the two phenyl rings. The Ni–P (2.126 Å) and Ni–Cl (2.201 Å) bonds are both shorter than those found[20] for

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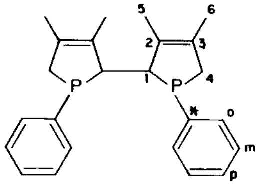
Table I. ^{1}H and ^{31}P{^{1}H} NMR Spectral Data for Biphospholene Derivatives[a]

compd[e]	δ(Ph)	δ(CH_3)	δ(CH)	δ(CH_2) (J_{HH}) H$_a$	δ(CH_2) (J_{HH}) H$_b$	δ(^{31}P)	Δδ(^{31}P)[b]
			R = Ph				
L	7.15–7.50	1.08, 1.81	2.60	3.30	2.80	−28.3	...
LO_2	7.50–7.80	1.80	2.70	3.60	2.80	49.26	77.56
LS_2	7.30–8.00	1.80	2.80	4.18 (11.4)	2.97 (11.4)	54.0	82.3
$LNiCl_2$	7.40–8.10	1.25, 1.80	3.31	3.66 (18)	3.66 (18)	80.0	108.3
$LNiBr_2$	7.30–8.15	1.26, 1.83	3.27	3.81 (18)	3.24 (18)	87.7	116
$LPdCl_2$	7.34–7.94	1.17, 1.75	3.57	3.60 (18)	3.20 (18)	88.3	116.6
$LPtCl_2$	7.20–8.00	1.13, 1.72	3.37	3.50 (18)	3.25 (18)	63.1[c]	91.3
trans-L_2RuCl_2	6.90–7.30	1.69, 1.73	3.18	3.58 (17.5)	2.75 (17.5)	81.0	109.3
			R = *t*-Bu				
L		0.85 (11.72)[d] (*t*-Bu) 1.67 (CH_3)	2.51	2.75 (18.7)	2.75 (18.7)	−5.39	
LS_2	...	1.20 (17.4)[d] (*t*-Bu) 1.62 (CH_3)	4.12	3.83 (18.7)	3.57 (18.7)	77.7	83.16
$LNiCl_2$		1.28 (14.9)[d] (*t*-Bu) 1.76 (CH_3)	3.39	3.16 (18.8)	2.70 (18.8)	103.10	108.49

[a] No attempt has been made to determine J_{PH} of these complex second-order spin systems. [b] $\Delta\delta(^{31}P) = \delta(^{31}P)_{complex} - \delta(^{31}P)_{ligand}$. [c] J_{PtP} = 3611 Hz. [d] $|^3J_{PH} + {}^5J_{PH}|$. [e] L = 2,2′-bis(1-R-3,4-dimethyl-2,5-dihydro-1*H*-phosphate).

Table II. ^{13}C NMR Data for Biphospholene Complexes (δ(^{13}C), Multiplicity, "J_{PC}" (Hz))[a] in $CDCl_3$



complex	C_1	C_2	C_3	C_4	C_5	C_6	C*	C_o	C_m	C_p	$^2J_{PP}$, Hz
$LNiCl_2$	57.9 t (51.3)	128.5 t (8.9)	131.3 t (5.9)	37.9 t (32.9)	14.1 t (6.1)	17.1 t (11)	129.6 t (43.8)	132.8 t (8.5)	128.7 t (9.8)	131.5 s	>50
$LNiBr_2$	58.5 t (51)	NO	131.6 t (6)	39.2 t (35.1)	14.1 t (6.8)	17.1 t (9.7)	NO	132.9 t (8.8)	128.7 t (10.7)	131.4 s	>50
$LPdCl_2$	58.3 5L (13.55, 36.55)	128.2 5L (−1.2, 12.2)	131.4 t (7.3)	37.8 5L (−1.02, 33.91)	13.8 5L (−0.38, 6.68)	17.1 5L (−1.17, 10.97)	128.6 d (46)	133.3 5L (−0.88, 11.77)	129.1 5L (−0.65, 11.65)	132.1 s	7.8
$LPtCl_2$	56.81 dd, (42.8, 8.6)[b]	128.10 d (9.8)	131.2 d (6.1)	36.8 d (40.3)[c]	13.8 d (7.4)	17.1 d (11)	129.3 d (46)	133.6 d (11)[d]	129.0 d (11)	132.3 d (2.3)	0
L_2RuCl_2[f]	60.0 5L (15.7)	128.5 d (15)	131.5 d (9)	36.4 5L (13.5)	16.8 s	17.0 s	138.3 5L (17.1)	131.1 s	128.0 s	128.2 s	NO
$L'NiCl_2$[e]	53.4 t (45.9)	129.5 s	131.8 s	33.5 5L (−3.49, 23.01)	16.12 5L (6)	17.25 d (3.9)					

[a] When only one value is given, it is for $|^nJ_{PC} + {}^{n+2}J_{PC}|$. Abbreviations: s ≡ singlet, d ≡ doublet, t ≡ triplet, 5L ≡ 5-line multiplet, NO = not observed. [b] J_{PtC} = 101.3 Hz. [c] J_{PtC} = 31.8 Hz. [d] J_{PtC} = 20.1 Hz. [e] L′ = 2,2′-bis(*tert*-butyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole); δ(*t*-Bu CH_3) = 28.17 s; δ(*t*-Bu tertiary C) = 24.53 (unresolved multiplet). [f] AXX′X″X‴ spin system; coupling constants given are the separations equivalent to the AXX′ spin.

Table III. Positional Parameters and Their Estimated Standard Deviations for **1**

atom	x	y	z	B,[a] Å^2
Ni	0.000	0.18140 (6)	0.250	2.63 (1)
Cl	−0.07919 (6)	0.03003 (8)	0.16103 (5)	4.42 (2)
P	0.04910 (5)	0.34125 (7)	0.33505 (4)	2.37 (1)
C1	0.0355 (2)	0.5179 (3)	0.2916 (2)	2.36 (5)
C2	0.1423 (2)	0.5584 (3)	0.2986 (2)	2.69 (6)
C3	0.2139 (2)	0.4788 (3)	0.3443 (2)	2.77 (6)
C4	0.1817 (2)	0.3543 (3)	0.3832 (2)	3.15 (6)
C5	0.1586 (2)	0.6910 (3)	0.2598 (2)	3.81 (7)
C6	0.3223 (3)	0.5043 (4)	0.3625 (3)	4.52 (8)
C7	−0.0168 (2)	0.3350 (3)	0.4089 (2)	2.63 (6)
C8	−0.1074 (2)	0.3979 (3)	0.3943 (2)	3.38 (6)
C9	−0.1617 (2)	0.3861 (4)	0.4479 (2)	3.89 (7)
C10	−0.1246 (2)	0.3103 (3)	0.5150 (2)	3.81 (7)
C11	−0.0359 (2)	0.2460 (4)	0.5299 (2)	3.83 (7)
C12	0.0196 (2)	0.2570 (4)	0.4765 (2)	3.57 (7)

[a] Anisotropically refined atoms are given in form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table IV. Positional Parameters and Their Estimated Standard Deviations for **3**

atom	x	y	z	B,[a] Å^2
Pd	0.31637 (3)	0.22319 (2)	0.20971 (5)	1.906 (9)
Cl1	0.2322 (1)	0.2593 (1)	0.4194 (2)	3.82 (4)
Cl2	0.4377 (1)	0.17509 (9)	0.3485 (2)	3.82 (3)
P1	0.2140 (1)	0.27603 (8)	0.0657 (2)	2.05 (3)
P2	0.38330 (9)	0.19447 (8)	−0.0032 (2)	2.16 (3)
C1	0.1053 (4)	0.2343 (4)	0.0734 (8)	3.2 (1)
C2	0.1105 (4)	0.1730 (4)	−0.0415 (7)	2.8 (1)
C3	0.1734 (4)	0.1791 (3)	−0.1429 (7)	2.6 (1)
C4	0.2303 (4)	0.2515 (3)	−0.1326 (7)	2.2 (1)
C5	0.0423 (5)	0.1129 (5)	−0.036 (1)	5.8 (2)
C6	0.1919(5)	0.1251 (4)	−0.2694 (8)	3.7 (2)
C7	0.3283 (4)	0.2415 (3)	−0.1644 (7)	2.2 (1)
C8	0.3797 (4)	0.3149 (3)	−0.1699 (7)	2.5 (1)
C9	0.4563 (4)	0.3160 (4)	−0.0967 (7)	2.8 (1)
C10	0.4866 (4)	0.2448 (4)	−0.0193 (9)	3.2 (1)
C11	0.3414 (5)	0.3785 (4)	−0.2598 (8)	3.7 (1)
C12	0.5180 (5)	0.3830 (4)	−0.0813 (9)	4.4 (2)
C13	0.2152 (4)	0.3770 (3)	0.0853 (7)	2.4 (1)
C14	0.2884 (5)	0.4104 (4)	0.1482 (8)	3.5 (1)
C15	0.2950 (5)	0.4871 (4)	0.1494 (9)	4.5 (2)
C16	0.2288 (6)	0.5307 (4)	0.0933 (9)	4.8 (2)
C17	0.1541 (6)	0.4979 (4)	0.0329 (8)	4.7 (2)
C18	0.1467 (5)	0.4205 (4)	0.0292 (8)	3.7 (2)
C19	0.3915 (4)	0.0962 (3)	−0.0429 (7)	2.3 (1)
C20	0.4460 (4)	0.0687 (4)	−0.1535 (8)	3.4 (1)
C21	0.4505 (5)	−0.0063 (4)	−0.1857 (8)	3.9 (2)
C22	0.3957 (5)	−0.0541 (4)	−0.1161 (9)	4.3 (2)
C23	0.3386 (5)	−0.0294 (4)	−0.0064 (9)	4.2 (2)
C24	0.3371 (4)	0.0464 (4)	0.0270 (8)	3.1 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as shown in Table III.

Table V. Selected Bond Lengths (Å) and Angles (deg) for LNiCl$_2$ (**1**)[a]

Ni–Cl	2.201 (1)
Ni–P	2.126 (1)
P–C1	1.852 (2)
P–C4	1.825 (2)
P–C7	1.817 (2)
C1–C1′	1.527 (4)
C1–C2	1.528 (3)
C2–C3	1.338 (3)
C2–C5	1.499 (3)
C3–C4	1.517 (3)
C3–C6	1.491 (4)
mean C–C (Ph ring)	1.377 (4)
Cl–Ni–Cl′	97.27 (4)
Cl–Ni–P′	169.08 (3)
Cl–Ni–P	88.46 (2)
P–Ni–P′	87.46 (3)
Ni–P–C1	113.10 (7)
Ni–P–C4	117.55 (8)
Ni–P–C7	111.10 (7)
C1–P–C4	95.8 (1)
C1–P–C7	108.6 (1)
C4–P–C7	109.5 (1)
P–C1–C1′	111.32 (8)
P–C1–C2	102.6 (1)
C1′–C1–C2	115.9 (2)
C1–C2–C3	117.4 (2)
C1–C2–C5	117.3 (2)
C3–C2–C5	125.1 (2)
C2–C3–C4	117.0 (2)
C2–C3–C6	125.9 (2)
C4–C3–C6	117.1 (2)
P–C4–C3	104.0 (2)

[a] The primed atoms are related to the unprimed atoms by the two-fold symmetry axis.

Table VI. Selected Bond Lengths (Å) and Angles (deg) for LPdCl$_2$ (**3**)

Pd–Cl1	2.369 (1)	Pd–Cl2	2.363 (1)
Pd–P1	2.210 (1)	Pd–P2	2.225 (1)
P1–C1	1.814 (5)	P1–C4	1.839 (5)
P1–C13	1.809 (5)	P2–C7	1.850 (5)
P2–C10	1.817 (5)	P2–C19	1.794 (5)
C1–C2	1.501 (8)	C2–C3	1.330 (7)
C2–C5	1.493 (8)	C3–C4	1.557 (6)
C3–C6	1.512 (7)	C4–C7	1.520 (6)
C7–C8	1.525 (7)	C8–C9	1.325 (7)
C8–C11	1.501 (7)	C9–C10	1.513 (8)
C9–C12	1.524 (7)	mean C–C (Ph ring)	1.377 (9)
Cl1–Pd–Cl2	96.52 (5)	Cl1–Pd–P1	87.53 (5)
Cl1–Pd–P2	173.61 (5)	Cl2–Pd–P1	173.41 (5)
Cl2–Pd–P2	89.86 (5)	P1–Pd–P2	86.10 (5)
Pd–P1–C1	115.82 (18)	Pd–P1–C4	110.5 (15)
Pd–P1–C13	111.25 (16)	C1–P1–C4	94.4 (23)
C1–P1–C13	114.35 (23)	C4–P1–C13	109.2 (21)
Pd–P2–C2	110.40 (16)	Pd–P2–C10	111.2 (20)
Pd–P2–C19	115.18 (17)	C7–P2–C10	95.4 (23)
C7–P2–C10	95.40 (23)	C7–P2–C19	108.8 (22)
C10–P2–C19	113.90 (24)	P1–C1–C2	102.4 (4)
P1–C1–C3	74.57 (21)	C1–C2–C3	116.8 (4)
C1–C2–C4	81.79 (30)	C1–C2–C5	117.2 (5)
C3–C2–C5	126.01 (54)	C2–C3–C4	115.6 (4)
C2–C3–C6	126.79 (46)	C4–C3–C6	117.5 (4)
P1–C4–C3	99.79 (31)	P1–C4–C7	110.6 (3)
C3–C4–C7	115.76 (40)	P2–C7–C4	109.7 (3)
P2–C7–C8	100.90 (31)	C4–C7–C8	114.0 (4)
C7–C8–C9	116.38 (43)	C7–C8–C11	118.2 (4)
C8–C9–C10	117.97 (44)	C8–C9–C12	126.5 (5)
C10–C9–C12	115.81 (45)	P2–C10–C9	101.2 (3)

cis-dichlorobis(1-benzyl-2,5-dihydro-1*H*-phosphole)nickel(II) (Ni–P = 2.155 Å, Ni–Cl = 2.216 Å). The latter compound also has a greater tetrahedral distortion than is found for the biphospholene complex. This can be seen by comparing the values of the dihedral angles between the P$_2$Ni and Cl$_2$Ni planes for these two compounds, which are 20.4° for the phospholene complex and 13.6° for the biphospholene complex. The palladium complex has a smaller P$_2$Pd/Cl$_2$Pd dihedral angle (5.2°), which is larger than that found[21] for Pd(dppe)Cl$_2$ (3°). The smaller tetrahedral distortion for the LPdCl$_2$ complex than for the LNiCl$_2$ complex is to be expected. The larger tetrahedral distortion of the LPdCl$_2$ complex compared to that for Pd(dppe)Cl$_2$ is a result of the rigidity of the biphospholene ligand. Since nickel has a small energy difference between tetrahedral and square-planar geometries, the overall molecule adopts a conformation that is controlled by the chelate ring in its most stable form, which is not far from planarity. By contrast, for palladium the square-planar geometry is much more stable and a greater puckering of the chelate ring results.

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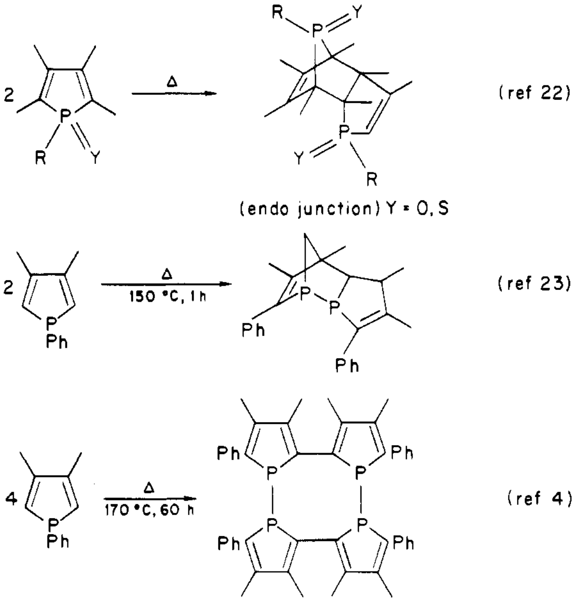
Scheme II

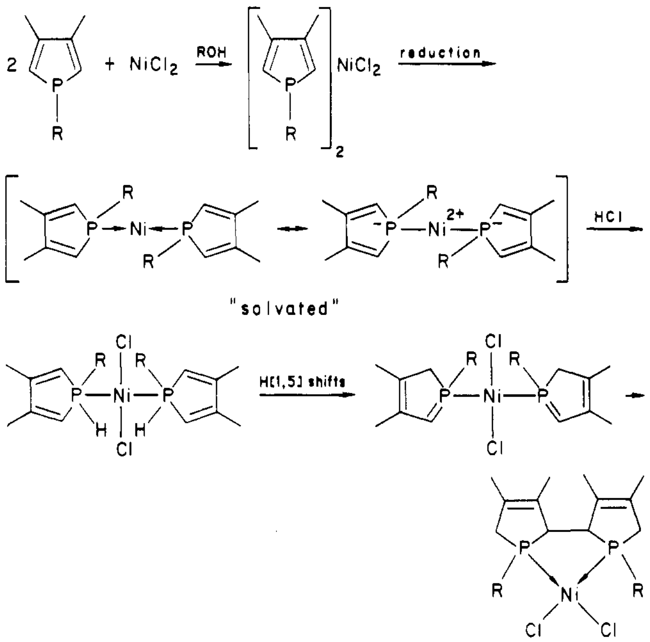


The puckering is considerably less and the tetrahedral distortion more than for Pd(dppe)Cl_2. All this suggests that the diphospholene ligand is a strong-donor, rigid, bidentate ligand. This is also supported by the Pd–P (2.218 Å) and Pd–Cl (2.366 Å) bond distances of the biphospholene complex being respectively shorter and longer than the Pd–P (2.230 Å) and Pd–Cl (2.359 Å) bond distances for Pd(dppe)Cl_2. The structures of the biphospholene ligand in the two complexes are otherwise very similar with no unusual bond distances or angles.

Because the diphospholene possesses acidic hydrogens adjacent to phosphorus, the basic sodium cyanide could cause epimerization of the ligand during the cyanide displacement. However, the ligand has the same conformation in the nickel and palladium complexes and the palladium complex is formed in very high yield. Thus, it appears that the ligand is not epimerized during the cyanide displacement. Molecular models suggest that there would be considerably greater steric repulsions between phenyl rings for the biphospholene ligand in the meso form than in the chiral form. Thus, the initial formation of the chiral form of the ligand on nickel and its transfer to other metals without epimerization is probably the result of steric effects.

Several experiments directed toward understanding the mechanism of reaction 3 have been conducted. This reaction occurs with both 1-phenyl- and 1-*tert*-butyl-3,4-dimethylphosphole with equivalent yield but not with 1-phenylphosphole. The first two form a variety of transition-metal complexes and have donor abilities roughly comparable to those of divinylphenylphosphine or dimethylphenylphosphine.[2] However, 1-phenylphosphole is so weak a donor that coordination to electron-deficient metals is very difficult.[2] Also, the thermolysis of phospholes in the absence of nickel(II) takes a completely different course[4] (Scheme II). Reaction 3 does not occur in the presence of either $PdCl_2$ or $PtCl_2$. Instead, in these two cases the classical phosphole complexes that we have previously described[24,25] are formed. Since reaction 3 appears to generally require an alcohol or other proton source, proton transfer from the solvent is likely. This has been verified by running the reaction in C_2H_5OD, where statistical deuterium labeling at both the methine and methylene groups of the diphospholene was observed. We have also attempted the reaction in *l*-menthol to see if asymmetric induction would result, but only a racemic product was obtained. Reaction 3 amounts to a reduction of the phosphole, and either the phosphole itself or the alcohol solvent[26] could conceivably serve as the reducing agent. Since no phosphole oxide was observed by ^{31}P NMR spectroscopy of the reaction solutions and a small (nonstoichiometric) amount of cyclohexanone was found when cyclohexanol was used as the solvent, we conclude that the alcohol is a reducing agent but that the biphospholene product is formed as the result of a catalytic cycle. We also observed the formation of trace amounts of elemental nickel and hydrogen in this reaction. A mechanism that is consistent with these observations is given in Scheme III.

Scheme III



The first point of this mechanism, i.e. formation of Ni(0) complexes from phosphines and Ni(II) halides, is a well-documented process;[27] the second point needs further examination. It involves an unprecedented addition of HCl onto a P→Ni bond. The formation of phosphoranide complexes is now well-documented.[28] The protonation of phospholes at phosphorus is now well-established.[29] Nevertheless, the proposed reaction needs to admit that the P→Ni bond is strongly polarized P^{δ}–$Ni^{\delta+}$, the rationale behind this being perhaps that the $P^{\delta-}$ phosphole unit acquires some additional stability through partial cyclic delocalization. In a similar vein, tetracoordinate phosphole anions

are probably involved during the attack of phospholes by alkyllithiums.[30] Additional evidence for this intermediate step is currently being sought. The third step (the H(1,5) shift) is now well-documented for the phosphole ring. (See the discussion in ref 31.) The last step involves the creation of a C–C bond from two P=C double-bonded units. This kind of reaction is exemplified by the [2 + 2] head to head dimerization of methylenephosphines.[32] This mechanism explains why this type of di-

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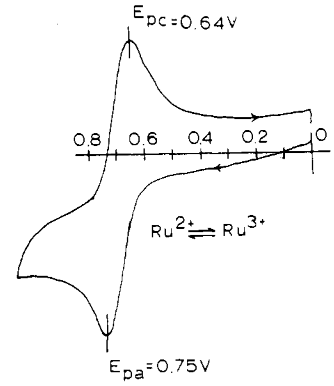

Figure 6. Cyclic voltammogram of t-L_2RuCl_2 in CH_3CN containing 0.1 M tetrahexylammonium perchlorate.

merization is specific of the phosphole system (third step) and why it works only with very basic phospholes (protonation of phosphorus). The specificity of nickel could be linked to the fact that *cis*-L_2Ni^0 complexes are easily formed but have, nevertheless, a high electronegativity, facilitating "reoxidation" by HCl addition onto the P→Ni bond. Of course, other metals have basically these same properties and we are currently seeking to extend this reaction by using some of these metals.

The ruthenium complex is a very stable molecule as shown by its electrochemistry. No reduction to lower valent ruthenium complexes could be observed in acetonitrile, but a reversible oxidation to Ru^{3+} occurs with $E_{1/2} = 0.70$ V, $E_{pc} = 0.64$ V, $E_{pa} = 0.75$ V, and $I_{pa}/I_{pc} = 1.0$ by cyclic voltammetry and $E° = 0.73$ V by stationary voltammetry (Figure 6). In contrast to *trans*-$(dppe)_2RuCl_2$, which isomerizes[33] to *cis*-$(dppe)_2RuCl_2$, the biphospholene analogue t-L_2RuCl_2 undergoes a reversible oxidation without isomerization. The oxidation potentials for the two complexes L_2RuCl_2 (0.73 V vs. SCE) and $(dppe)_2RuCl_2$ (0.79 V vs. SCE) are very similar, suggesting similar donor abilities for the two ligands.

Similar cyclic voltammetry studies on the $LNiCl_2$ and $LPdCl_2$ complexes showed the $LNiCl_2$ complex to undergo an irreversible two-electron oxidation ($E_{pc} = 1.0$, $E_{pa} = 1.25$ V) and an irreversible two-electron reduction ($E_{pc} = -1.08$ V, $E_{pa} = -0.6$ V) as did the $LPdCl_2$ complex (oxidation, $E_{pc} = 0.95$ V, $E_{pa} = 1.45$ V; reduction, $E_{pc} = -1.45$ V, $E_{pa} = -0.6$ V). These irreversible electrochemical reactions are probably due to the chemical events

$$LMCl_2 + 2e^- \rightarrow M^0 + L + 2Cl^- \quad \text{reduction}$$

$$LMCl_2 \rightarrow M^{2+} + L^{2+} + 2Cl^- + 2e^- \quad \text{(oxidation)}$$

Further chemistry of this new ligand system including the use of these complexes as homogeneous catalysts is currently under investigation.

Experimental Section

A. General Considerations. NMR spectra (chemical shifts in ppm from internal Me_4Si for ^1H and ^{13}C and from external 85% H_3PO_4 for ^{31}P; δ is positive for downfield shifts in all cases) were recorded on Bruker WP-80, WP-200, JEOL FX-100, and Nicolet QN300 spectrometers in the FT mode. Mass spectra were recorded on a MS30AEI spectrometer at 70 eV. Elemental analyses were performed by Service Central d'Analyse de CNRS, Lyon, France. Infrared spectra were recorded on Perkin-Elmer 499 and 599 instruments as KBr disks and on a Polytec FIR 30 FT interferometer as polyethylene disks. Electrochemical studies were conducted[34] with a platinum rotating-disk electrode (area 3.14 mm^2) in CH_3CN containing 0.1 M tetrahexylammonium perchlorate. The CH_3CN was freshly distilled under argon. Measurements were performed with a Bruker E130M potentiostat associated with a high-impedance MV-meter (Tacussel, Minisis 6000) and an Ifelec 3802 X-Y recorder. A three-electrode system was used involving platinum working and auxiliary electrodes and a saturated calomel electrode as reference, the latter being in electrical contact with the cell through a junction bridge filled with CH_3CN and Hx_4NClO_4. No ohmic drop correction was made as preliminary experiments on Fc/Fc$^+$[35] demonstrated that cyclic voltammetry led to acceptable values of k_s. Conductivity studies were carried out at 25 ● 0.1 °C. Temperature regulation was achieved with a Brinkman Lauda K-2/R temperature controller. Conductance measurements were made by using a Yellow Springs Instruments conductivity cell, Model No 3403, and measured with an Industrial Instruments conductivity bridge, Model RC16B2, which was adapted for use with a Tektronix Type 310 oscilloscope. All the complexes are nonelectrolytes. The phospholes were prepared as previously described,[36] and all reactions were performed under an atmosphere of either argon or nitrogen. Chromatographic separations were performed on silica gel columns (70–230 mesh, Merck).

B. Synthesis. 1. Dichloro[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II). Method A. A mixture of 20.46 g (0.1080 mol) of 1-phenyl-3,4-dimethylphosphole,[36] 7.00 g (0.054 mol) of anhydrous $NiCl_2$ (Merck), and 100 mL of cyclohexanol was heated with vigorous magnetic stirring under a dry nitrogen atmosphere at 140 °C for 24 h. Dark red crystals of product began to appear around the edge of the flask after 1 h. After 24 h of heating, some black solid (Ni(0)) was also evident in the reaction mixture. The cyclohexanol was removed under vacuum at 100 °C and treated with (2,4-dinitrophenyl)hydrazine to produce 0.4 g of cyclohexanone (2,4-dinitrophenyl)hydrazone (yellow crystals, mp 161–163 °C, lit.[37] mp 162 °C). The residue was allowed to cool to room temperature to produce a deep red solid. This solid was crushed, washed with 100 mL of absolute ethanol, and dissolved in 500 mL of dry purified dichloromethane and the deep red solution filtered to remove some insoluble black material. To the filtrate was added 100 mL of absolute ethanol, and the solution was reduced to 150 mL on a rotary evaporator at 50 °C and left standing at room temperature overnight. The resultant red crystalline product was isolated by filtration, washed with anhydrous diethyl ether, recrystallized from $CHCl_3$/C_2H_5OH, and vacuum-dried to afford 8.03 g (29.3%) of $LNiCl_2$, dec pt 306–308 °C. Anal. Calcd for $C_{24}H_{28}Cl_2NiP_2$: C, 56.74; H, 5.55; Ni, 11.55; Cl, 13.96; P, 12.19. Found: C, 56.68; H, 5.65; Ni, 10.98; Cl, 14.21; P, 11.94.

Method B. A mixture of 6.69 g (0.0265 mol) of $NiCl_2 \cdot 6H_2O$, 10 g (0.053 mol) of 1-phenyl-3,4-dimethylphosphole, and 100 mL of absolute ethanol was stirred vigorously and refluxed under dry nitrogen for 3 h. The initially deep green solution began to deposit red crystals of dichlorobis(1-phenyl-3,4-dimethylphosphole)nickel(II)[38] after 1-h reflux. The solution was cooled to room temperature under nitrogen, and the red-brown solid was isolated by filtration under nitrogen, washed with anhydrous diethyl ether, and vacuum-dried. To this solid was added 50 mL of cyclohexanol and the mixture heated with vigorous stirring at 140 °C for 32 h under dry nitrogen. Removal of the cyclohexanol under vacuum, isolation, and purification as above, afforded 2.07 g (15.4%) of red-orange crystals, dec pt 306–308 °C. Mass spectrum (*m/e* (relative intensity)): 508 (M, 2.5), 378 (M − $NiCl_2$, 12), 266 (57), 189 (L/2, 100). IR (cm^{-1}): ν_{NiCl} 341, 317; ν_{NiP} 404, 386; $\nu_{C=C}$ 1660.

This complex can also be prepared by method A using anhydrous nickel(II) chloride in benzonitrile, 2-methoxyethanol, *n*-butyl alcohol, tert-butyl alcohol, or *l*-menthol, but attempts with hydrated nickel(II) chloride in ethylene glycol or cyclohexanol/ethanol failed.

2. Dichloro[2,2′-bi(1-*tert*-butyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II) was prepared in 29% yield by method A using 1-*tert*-butyl-3,4-dimethylphosphole[36] red crystals, dec pt 268–270 °C. Mass spectrum (*m/e* (relative intensity)): 468 (M, 62); 433 (M − Cl, 100); 397 (M − 2 Cl, 30); 281 (M − *t*-Bu, 45); 169 (M/2, 33). Anal. Calcd for $C_{20}H_{36}Cl_2NiP_2$: C, 51.46; H, 7.71; Cl, 15.19; Ni, 12.58; P, 13.07. Found: C, 50.67; H, 7.72; Cl, 15.47; Ni, 11.13; P, 11.63.

3. Dibromo[2,2-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II). A mixture of 18.8 g (0.1 mol) of 1-phenyl-3,4-dimethylphosphole,[36] 10.94 g (0.05 mol) of anhydrous $NiBr_2$ (Aldrich), and 40 mL of benzonitrile was heated at 160 °C for 48 h under argon. Following cooling to room temperature, the benzonitrile was removed under vacuum, the dark red residue was washed with 100 mL of hexane and 100 mL of anhydrous diethyl ether and dissolved in 250 mL of dichloromethane, and the deep red solution was filtered. The filtrate was reduced in volume to 25 mL, and 50 mL of absolute ethanol was added. After the mixture stood at room temperature overnight, the red crystals

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were isolated by filtration, washed with anhydrous diethyl ether, and vacuum-dried to yield 2 g (6.7%) of deep red crystals of the title compound, dec pt 284–286 °C. In a procedure as above but with 2-methoxyethanol as solvent, the yield was 16.2%. Anal. Calcd for $C_{24}H_{28}Br_2NiP_2$: C, 48.31; H, 4.69; Br, 26.78; Ni, 9.84; P, 10.38. Found: C, 48.13; H, 4.79; Br, 26.98; Ni, 9.68; P, 9.77. IR (cm^{-1}): ν_{NiBr} 279.5, 299; ν_{NiP} 372.5, 399.5.

4. **2,2′-Bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole).** To a solution of 500 mg (0.98 mmol) of recrystallized dichloro[2,2′-bi[1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II) in 25 mL of dry dichloromethane was added 10 mL of saturated aqueous sodium cyanide solution (100 g/L) under nitrogen, and the mixture was stirred vigorously for 1 h to produce a nearly colorless CH_2Cl_2 phase and a yellow-orange aqueous phase. The CH_2Cl_2 layer was separated, dried over anhydrous sodium sulfate, and chromatographed under N_2 on silica gel with toluene under nitrogen to afford 350 mg (92%) of biphospholene as a colorless, viscous, very air-sensitive liquid. This compound was characterized by ^1H and ^{31}P NMR (Table I) and as its dioxide and disulfide (vide infra).

5. **2,2′-Bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole 1-oxide).** To a solution of 5 g (9.8 mmol) of crude dichloro[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II) in 50 mL of CH_2Cl_2 was added 20 mL of saturated aqueous sodium cyanide (100 g/L). This mixture was stirred vigorously in the air for 1 h, and the CH_2Cl_2 layer was separated, washed with water (100 mL), dried over anhydrous sodium sulfate, and evaporated to dryness to afford 2.7 g of an oily mixture of biphospholene and biphospholene dioxide. These were separated by column chromatography on silica gel (ethyl acetate/ethanol (90:10) eluent) to afford 1.2 g (30%) of the title compound, mp >250 °C. Mass spectrum (*m*/*e* (relative intensity): 410 (M, 12), 205 (M/2, 100). IR (cm^{-1}): $\nu_{P=O}$ 1195; $\nu_{C=C}$ 1655. Anal. Calcd for $C_{24}H_{28}P_2O_2$: C, 70.27; H, 6.83; P, 15.10; O, 7.80. Found: C, 69.48; 69.44; H, 6.38, 6.51; P, 13.49; 13.59; O, 7.80, 7.50.

6. **2,2′-Bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole 1-sulfide).** To a solution containing 2.5 g (4.9 mmol) of crude dichloro[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II) in 100 mL of benzene was added 25 mL of saturated aqueous sodium cyanide solution under argon. This mixture was stirred vigorously at room temperature for 5 min, 200 mg of S_8 was added, and the mixture was heated at 60 °C for 1 h. The resulting solution was filtered, and the benzene layer was separated, washed with water (100 mL), dried over anhydrous sodium sulfate, and chromatographed rapidly on silica gel (toluene/ethyl acetate (80:10) eluent) to obtain 1.2 g of crude product. A second chromatography on silica gel (toluene/ethyl acetate (90:10) eluent) afforded 900 mg (40%) of the title compound, mp 218 °C. Mass spectrum, (*m*/*e* (relative intensity)): 442 (M, 100), 221 (M/2, 40), 189 (26). IR (cm^{-1}): $\nu_{P=S}$ 610; $\nu_{C=C}$ 1655. Anal. Calcd for $C_{24}H_{28}P_2S_2$: C, 65.21; H, 6.38; P, 14.02. Found: C, 64.93; H, 6.27; P, 13.93.

7. **Dichloro[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]palladium(II).** To a solution containing 1.00 g (1.97 mmol) of pure dichloro[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II) in 200 mL of CH_2Cl_2 was added 200 mL saturated aqueous potassium cyanide solution under nitrogen. The mixture was agitated vigorously with a stream of dry nitrogen for 1 h until the CH_2Cl_2 layer was colorless and the aqueous phase yellow-orange. The CH_2Cl_2 phase was separated and filtered through Celite and anhydrous sodium sulfate under nitrogen. To the filtrate was added 0.511 g (1.97 mmol) of dichlorobis(acetonitrile)palladium(II) and the mixture stirred under nitrogen for 2 h. The solid product was separated by filtration and stirred with gentle heating overnight in absolute ethanol. After the mixture was cooled to room temperature, addition of anhydrous diethyl ether afforded 0.973 g (62%) of pale yellow crystals, dec pt 276 °C. IR (cm^{-1}): ν_{PdCl} 276.5, 302; ν_{PdP} 407, 371; $\nu_{C=C}$ 1675, 1650. Anal. Calcd for $C_{24}H_{28}Cl_2P_2Pd$: C, 51.89; H, 5.04; Cl, 12.76. Found: C, 51.74, 51.75; H, 5.03, 5.20; Cl, 14.03, 14.33. Attempts to prepare this same complex by thermolysis of *cis*-dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II) in cyclohexanol or by heating of palladium chloride, $Pd(C_6H_5CN)_2Cl_2$, or $Pd(CH_3CN)_2Cl_2$ with 1-phenyl-3,4-dimethylphosphole in a variety of solvents did not produce the same compound.

8. **Dichloro[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]platinum(II).** Proceeding as in preparation 7 but using 0.685 g (1.97 mmol) $Pt(CH_3CN)_2Cl_2$ afforded 0.9 g (70.98%) pale yellow crystals of the title compound dec. pt 226–229 °C. I.R. ν_{PtCl}, 285.5, 306; ν_{PtP}, 407, 389, $\nu_{C=C}$, 1630 cm^{-1}. Anal. Calcd for $C_{24}H_{28}Cl_2P_2Pt$: C, 44.75; H, 4.35; Cl, 11.01. Found: C, 44.62; 44.65; H, 4.33; Cl, 11.13, 11.03.

9. ***trans*-Dichlorobis[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]ruthenium(II).** A solution of 2 g (3.938 mmol) pure dichloro[2,2′-bi(1-phenyl-3,4-dimethyl)-2,5-dihydro-1*H*-phosphole)]nickel(II) in 200 mL of CH_2Cl_2 was treated with 100 mL of saturated aqueous potassium cyanide under nitrogen for 1 h. The CH_2Cl_2 layer was separated, filtered through Celite and anhydrous sodium sulfate, and added to 1.88 g (1.97 mmol) of $(Ph_3P)_3RuCl_2$ under nitrogen. After this solution was stirred at room temperature for 1 h, the solution was reduced in volume to 75 mL on rotary evaporator and 200 mL anhydrous diethyl ether was added. This mixture was allowed to stand at room temperature overnight, and the large translucent pale yellow crystals were isolated by filtration, washed with anhydrous diethyl ether, and air-dried to afford 1.0 g (54.6%) of the title compound, dec pt >340 °C. IR (cm^{-1}): ν_{RuCl}, 321.5, ν_{RuP} 390, 402; $\nu_{C=C}$ 1660. Anal. Calcd for $C_{48}H_{56}Cl_2P_4Ru$: C, 62.10; H, 6.03; Cl, 7.64. Found: C, 62.32; H, 6.03; Cl, 7.22, 7.43.

10. **2,2′-Bi(1-*tert*-butyl-3,4-dimethyl-2,5-dihydro-2*H*-phosphole-3-ene).** Treatment of the nickel(II) chloride complex prepared in synthesis 2 with dichloromethane and a saturated aqueous sodium cyanide solution under argon as in synthesis 4 afforded an 80% yield of a colorless, very air-sensitive viscous liquid after chromatography on silica gel under argon (toluene eluent). This compound was characterized by ^1H and ^{31}P NMR (Table I) and as its disulfide.

11. **2,2′-Bi(1-*tert*-butyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole 1-sulfide).** Reaction of the biphospholene prepared by synthesis 10 with sulfur in benzene for 1 h at 60 °C afforded the title compound in 80% yield as colorless crystals, mp >260 °C. Mass spectrum (*m*/*e* (relative intensity)): 402 (M, 100), 201 (M/2, 5). IR (cm^{-1}): $\nu_{P=S}$ 605; $\nu_{C=C}$ 1650 cm^{-1}. Anal. Calcd for $C_{20}H_{36}P_2S_2$: C, 59.71; H, 8.95; P, 15.40; S, 15.94. Found: C, 59.54, 59.88; H, 8.83, 8.92; P, 14.45, 14.60; S, 15.57, 15.32.

12. **[2,5,5-Trideuterio-2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II).** This reaction was carried out as in synthesis 1; 1-phenyl-3,4-dimethylphosphole was reacted with anhydrous nickel(II) chloride in CH_3CH_2OD in a sealed tube at 160 °C for 6 h. The complex was isolated and converted to the disulfide as in synthesis 6. The disulfide was analyzed by ^{31}P and ^1H NMR, the latter showing by integration a 50% labeling of positions 2 and 5 of the ring. The mass spectrum of the nickel complex showed *m*/*e* (relative intensity) 511 (M, 60), 474 (M − HCl, 50), 435 (35), 190 (M/2, 10), 83 (100).

C. X-ray Data Collection and Processing. Crystals of $LNiCl_2$ (**1**) and $LPdCl_2$ (**2**) were obtained by slow evaporation of CH_2Cl_2/C_2H_5OH solutions at room temperature. A dark red 0.22 × 0.20 × 0.08 mm parallelepiped of **1** and a very pale yellow 0.26 × 0.09 × 0.09 mm parallelepiped of **2** were sealed in Lindemann glass capillaries and mounted on rotation-free goniometer heads. All quantitative data were obtained from a Philips PW1100/16 four-circle automatic diffractometer, controlled by a P852 computer, using graphite-monochromated radiation. Systematic searches in reciprocal space showed that both crystals belong to the monoclinic system. The unit cell dimensions and their standard deviations were obtained and refined at room temperature with Cu K α radiation (λ = 1.5418 Å) by using 25 carefully selected reflections and the standard Philips software. Final results: $C_{24}H_{28}P_2Cl_2Ni$, mol wt 507.81, a = 14.127 (5) Å, b = 9.611 (3) Å, c = 17.777 (6) Å, β = 106.81 (2)°, V = 2310 Å^3, Z = 4, ρ_{calcd} = 1.455 g cm^{-3}, ρ_{obsd} = 1.43 ± 0.02 g cm^{-3}, μ = 47.78 cm^{-1}, F_{000} = 1048, space group $C2/c$; $C_{24}H_{28}P_2Cl_2Pd$, mol wt 555.5, a = 15.199 (3) Å, b = 17.844 (4) Å, c = 8.900 (2) Å, β = 90.97 (2)°, V = 2413 Å^3, Z = 4, ρ_{calcd} = 1.518 g cm^{-3}, ρ_{obsd} = 1.49 ± 0.02 g cm^{-3}, μ = 97.87 cm^{-1}, F_{000} = 1112, space group $P2_1/n$.

The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2σ level. The total scan width in the $\theta/2\theta$ flying step scan used was $\Delta\theta = 0.9 +$ (Cu K$\alpha_{1,2}$ splitting) by 0.143 tan θ with step widths of 0.04° for **1** and 0.05° for **2** and scan speeds of 0.020° s^{-1} for **1** and 0.024° s^{-1} for **2**. Totals of 3529 $h,\pm k,\pm l$ reflections (**1**) and 3471 $h,k,\pm l$ reflections (**2**) were recorded (5° < θ < 57°). The resulting data sets were transferred to a PDP 11/60 computer, and for all subsequent computations, the Enraf-Nonius SDP/V18 package was used[39] with the exception of a local data-reduction program.

Three standard reflections measured every hour during the entire data-collection periods showed no significant trends. The raw step-scan data were converted to intensities with use of the Lehmann–Larson method[40] and then corrected for Lorentz, polarization, and absorption factors, the last computed by the numerical integration method of Busing and Levy[41] (transmission factors between 0.36 and 0.67 (**1**) and between 0.21 and 0.47 (**2**)). Unique data sets of 1486 ($R_i(f)$ = 0.013) (**1**) and 2840 (**2**) reflections having $I > 3\sigma(I)$ were used for determining and refining the structures.

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The structures were solved with use of the heavy-atom method. After refinement of the heavy atom, difference-Fourier maps revealed maxima of residual electronic density close to the positions expected for hydrogen atoms. They were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors of 5 Å^2 (**1**) and 6 Å^2 (**2**) but not refined. Full least-squares refinement converged to $R(F) = 0.041$ and $R_w(F) = 0.078$ (**1**) and $R(F) = 0.056$ and $R_w(F) = 0.074$ (**2**) ($w = 1/\sigma^2(\text{count}) + (\rho I)^2$ (132 variables for **1** and 262 for **2**). The unit-weight observations were 1.87 for $\rho = 0.08$ (**1**) and 1.74 for $\rho = 0.08$ (**2**). Final difference Fourier maps revealed no significant maxima. Tables III and IV list the atomic positional and thermal parameters for all non-hydrogen atoms with their estimated standard deviations.

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Supplementary Material Available: Listings of atomic positional parameters for hydrogen atoms, observed and calculated structure factors, and thermal parameters for anisotropically refined atoms (U_{ij}) (24 pages). Ordering information is given on any current masthead page.

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Molecular Mechanics of High-Order Bonds

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Molecular mechanics was used to study the characteristics of homonuclear quadruple bonds between Cr, Mo, W, and Re atoms. Derived force constants that are consistent with the M–M stretching frequencies observed in $M_2(CH_3)_8^{4-}$ anions were used to calculate the barriers to rotation about quadruple bonds and to estimate the δ contribution to the Cr–Cr quadruple-bond strength, obtained as 11 kcal/mol. Satisfactory descriptions of the relationships between dimetal quadruple and triple bonds, in terms of their relative flexibilities and steric requirements of the ligands, were obtained.

Introduction

Chemical interaction between neighboring transition-metal atoms in molecules is remarkably diverse and variable, ranging from simple van der Waals interaction to quadruple bonding, which implies the overlap of four orbital pairs at the dimetal center. This variation from 0 to 4 in bond order is not necessarily matched by a parallel variation in observed structural properties, probably because of the extreme flexibility of metal–metal bonds in comparison with the more conventional covalent bonds formed between p-block atoms. Consequently, the experimental study of dimetal centers with high-order bonding often produces results that are in apparent contradiction or are difficult to interpret. The aim of the present work is to identify experimentally observed structural features in dimetal systems, ostensibly at variance with the trends predicted on the basis of bond order only, and to investigate the possibility of accounting for the discrepancies by the method of molecular mechanics. It, more specifically, deals with trends in vibrational frequency, dimetal bond length, and the conformational demands of δ bonding.

It is notoriously difficult to understand the variability of observed M–M vibrational frequencies, as for instance in compounds containing quadruply bonded dimolybdenum, conveniently formulated as $M\overset{4}{-}M$. In particular, one finds quadruple bonds between metal atoms in two basically different types of environment, exemplified by molybdenum carboxylates and terminally substituted dimolybdenum species, respectively. Metal–metal bonds of the first kind are bridged by bidentate ligands whereas only terminal ligands are present in compounds of the second kind. Although the bond order is the same in the two situations, one finds an average shift of about 30–90 cm^{-1} in stretching frequency ($\bar{\nu}$) between the two types,[1] $\bar{\nu}$ being uniformly less for unsupported bonds. A tentative explanation is provided by the calculation[2] that carboxylate-type bridging causes mixing of vibrational modes, but this is not clearly supported by experiment.[3]

Observed dimetal bond lengths offer a special interpretational challenge in that the observed ranges for different bond orders overlap almost at random.[4] A baffling example of this phenomenon emerges from a comparison of the W–W bond lengths in the propanoate $W_2(O_2CEt)_4$ and the axially substituted propanoate $W_2(O_2CEt)_4 \cdot 2CH_2Ph$, respectively. Despite the different bond orders of $W\overset{4}{-}W$ and $W\overset{3}{-}W$ and apart from the axial ligands in the triply bonded species, the two molecules have virtually identical structures.[5]

A quadruple bond is theoretically stabilized by δ overlap, which demands eclipsing of terminal ligands across the unbridged bond, despite the steric strain expected for this arrangement. The δ contribution should therefore be sufficient to overcome the steric barrier to rotation[6] and to stabilize the eclipsed conformation relative to the sterically more favorable staggered conformation. The compound $Re_2Cl_4(PEt_3)_4$, with a dimetal bond order of 3 however, also has eclipsed geometry, but certainly not stabilized by δ overlap. Eclipsing across the triple bond is therefore not due to electronic factors and can only be of steric origin. Simple steric arguments should therefore clearly distinguish between the two types of eclipsed conformation in order to support the theory of δ bonding.

It is proposed to analyze the interpretational problems described above by the methods of molecular mechanics as recently applied[7] to rationalize structural trends in dimetal systems of low bond order. This will provide a direct quantitative estimate of all intermolecular steric interactions and by implication a means of identifying electronic effects.

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