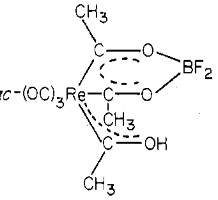
with the appearance of two singlets at δ 2.71 and 2.69 of relative intensity of ca. 2:1, respectively. This species may be the expected dienolic tautomer, but the isolation of this compound was not possible due to its low thermal stability (the half-life of this species at 25 °C is ca. 5 min). When a solution of this protonated species is treated with BF_3, the boron fluoride complex **3** is formed along with a very small amount of another yellow product which has been tentatively assigned structure **8** on the basis of the proton NMR, IR and mass spectral data.[11] Complex **8** is a (methyl)(hydroxy)carbenoid analogue to the (rhenaacetylacetonato)BF_2 complex.[4]



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The boron halide complexes, **3**–**6**, represent an unusual electronic structure for neutral, four-coordinate boron complexes. The boron atom is bonded formally to two anionic oxygen donor atoms and the anionic halide atom, while the fourth coordination site is occupied by a neutral, oxygen atom which is acting as an adduct molecule. However, the potential for electronic delocalization within the tripodal rhenium ligand apparently makes all three oxygen donor atoms equivalent to one another while maintaining a formal neutral charge on the boron atom. When the high thermodynamic stability of boron–oxygen bonds and the increased stability from the chelate effect of the vicinal, bifurcated rhenium ligand are considered, the boron halide complexes, **3**–**6**, may exhibit reaction chemistry more typical of a halo triorthoformate ester, $(RO)_3CX$. Since the tripodal rhenium ligand may not be displaced easily by an incoming nucelophile, we expect that these complexes should exhibit primarily S_N1 types of reaction chemistry.

As expected, the Finkelstein substitution reaction was unsuccessful when using complexes **4** and **5**. However, a silver ion assisted, ligand-exchange reaction did occur with complex **5** in alcoholic solution to afford the boron alkoxide complexes, **9**–**11**. The ligand-exchange reaction does not occur with secondary or tertiary alcohols.

$$\mathbf{5} + AgBF_4 \xrightarrow{ROH} [\mathit{fac}\text{-}(OC)_3Re(CH_3CO)_3]B(OR) + AgBr\downarrow + \{HBF_4\}$$

$$\mathbf{9},\ R = CH_3$$

$$\mathbf{10},\ R = CH_3CH_2$$

$$\mathbf{11},\ R = n\text{-}C_3H_7$$

These boron alkoxide complexes are yellow solids which are extremely difficult to separate from complex **5** by crystallization due to the high solubility of both types of complexes in organic solvents. Only the boron methoxide complex, **9**, could be isolated as an analytically pure solid. The proton NMR spectra of the reaction solutions indicate a bromide to alkoxide conversion of 90, 80, and 55% for **9**, **10**, and **11**, respectively. This variation in yield may be related to the decrease in the Brønsted acidities of the alcohols.

The carbonyl stretching vibrations of these complexes are essentially identical with those of the boron halide complexes, **3**–**6**. The proton resonances of the alkoxide ligand are shifted significantly to lower field from those resonances of either the free alcohol or the corresponding trialkylborate ester. This shift is a diagnositc indication of the formation of the rhenaboron alkoxide complexes and is probably due to the high electronegativity of the $(OC)_3Re$ moiety.

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Registry No. **1**, 69439-96-9; **3**, 73199-27-6; **4**, 73199-28-7; **5**, 73199-29-8; **6**, 73199-30-1; **8**, 73230-61-2; **9**, 73199-31-2; **10**, 73199-32-3; **11**, 73199-33-4; acetylpentacarbonylrhenium, 23319-44-0; BI_3, 13517-10-7; BBr_3, 10294-33-4; BCl_3, 10294-34-5; BF_3, 7637-07-2; 1-propanol, 71-23-8; ethanol, 64-17-5; methanol, 67-56-1.

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[11] IR (C_6H_{14}): ν(CO) 2030 (s), 1958 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): τ 7.34 (s, 3, CH_3), 7.36 (s, 6, 2 CH_3). Mass spectra: molecular ion peak at *m*/*e* 449 with the correct isotopic pattern.

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1,3-Butadienylphosphines and Some of Their Complexes

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The key roles of tervalent phosphorus derivatives and conjugated dienes as ligands in transition-metal chemistry are well-known. However only few complexes in which these two coordinating sites are linked within the same ligand have been described in the literature.[1–3] Such a paucity is partly due to the fact that free tervalent phosphorus derivatives of conjugated dienes are almost unknown.[4] In view of the various possibilities offered by such ligands in coordination chemistry (chelation, reversible exchange with free dienes, bridged complexes, etc.), we have launched a general study of (*Z*)- and (*E*)-1,3-butadienylalkylphosphines

$$>C=\overset{|}{C}-\overset{|}{C}=C-(CH_2)_nP^{III}<$$

A first paper was devoted to the synthesis of the (*Z*) compounds for $n = 2$.[7] The work reported hereafter describes the synthesis of (*E*)-1,3-butadienylphosphines ($n = 0$) and includes a preliminary study of their complexes with molybdenum and iron carbonyls.

Results and Discussion

Synthesis of (*E*)-1,3-Butadienylphosphines. One member of that family has been superficially described,[6] but its synthesis lacked generality. Since numerous syntheses of (*Z*)- and (*E*)-1,3-butadienylphosphoryl compounds were available,[8–20] a logical approach was to reduce the P=O bond of

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[2] W. Winter, *Angew. Chem., Int. Ed. Engl.*, **15**, 241 (1976).

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[4] As far as we know only two compounds in which a phosphino group is directly bonded to a conjugated diene are described in the literature, namely, 2-(diphenylphosphino)-1,3-butadiene[5] and 1-(diphenylphosphino)-4-phenyl-1,3-butadiene.[6] In both cases their characterization was minimal.

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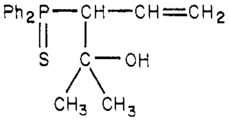
such species. However all our preliminary attempts[18] resulted in diene polymerization or hydrogenation. The reagents used for that purpose included $LiAlH_4$, $HSiCl_3$, $PhSiH_3$, and Si_2Cl_6. It was obvious that only a very mild reduction procedure could afford the desired phosphines. Thus we decided to use the nickelocene reduction–complexation of P=S bonds which was developed by us previously for such difficult cases.[21,22] Our approach is depicted in Scheme I.

The condensation of the carbonyl compounds onto the delocalized anion of allyldiphenylphosphine sulfide takes place almost exclusively on the γ-carbon.[23] Some α condensation was noted only in the case of acetone to give **6** which was



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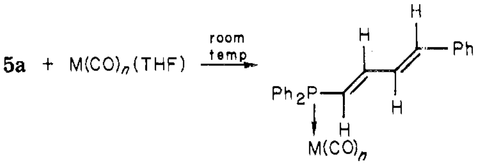
separated from **2c** by column chromatography and fully characterized (yield 5.4%).

That compounds **2a–c** are the (*E*) isomers was demonstrated unambiguously by a detailed 100-MHz $^1H\{^{31}P\}$ NMR study of **2a**. The two olefinic protons form an ABX system with $^3J(A-B) = 16.5$ Hz. The magnitude of the coupling constant implies a trans disposition. On the other hand the (*E,E*) structure of **3a** is only postulated (the ^1H NMR spectrum is very complicated) but is very likely since E1 eliminations give predominantly the less hindered isomer. We shall discuss further this point in the next section.

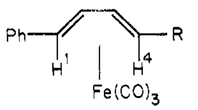
Complexes of (*E*)-1,3-Butadienylphosphines. All the experiments were performed with phosphine **5a**. The *P* complexes of **5a** with metal carbonyls were readily obtained by using classical procedures. Two such complexes **7** and **8** are described.



7, $M(CO)_n = Fe(CO)_4$ (yield 24%)
8, $M(CO)_n = Mo(CO)_5$ (yield 66.5%)

The iron tetracarbonyl complex **7** was also obtained directly in 36% yield by reacting phosphine sulfide **3a** with $Fe_3(CO)_{12}$ in boiling toluene. Such reduction–complexation reactions of P^{IV}=S bonds by iron carbonyls have been previously described in the literature.[24]

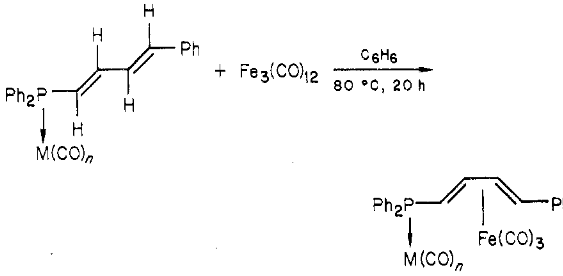
Table I. Comparison of ^1H NMR Data[a] of Some η^4-(4-R-1-phenyl-1,3-butadiene)iron Tricarbonyl Complexes



R	H^1 δ (*J*)	H^4 δ (*J*)	ref
H	1.66–2.67[e]	0.55 (9)	*b*
C_2H_5	1.95 (9)	*f*	*c*
CN	2.30 (9)	0.72 (7)	*d*
$Ph_2P \rightarrow Fe(CO)_4$ (9)	1.83 (8.6)	1.40 (10.3), $^2J(H-P) = 5.7$	this work
$Ph_2P \rightarrow Mo(CO)_5$ (10)	2.06 (9)	1.33 (8.5), $^2J(H-P) \approx 3$	this work

[a] δ in ppm, $^3J(H-H)$ in Hz; C_6D_6 + internal Me_4Si for complexes 9 and 10. [b] J. M. Landesberg and L. Katz, *J. Organomet. Chem.*, **35**, 327 (1972). [c] R. E. Graf and C. P. Lillya, *ibid.*, **122**, 377 (1976). [d] J. S. Frederiksen, R. E. Graf, D. G. Gresham, and C. P. Lillya, *J. Am. Chem. Soc.*, **101**, 3863 (1979). [e] Obscured by R = H. [f] Obscured by CH_3 at 1.07.

The dienic moieties of complexes **7** and **8** can also be engaged in a η complexation. Thus when reacting with $Fe_3(CO)_{12}$ in boiling benzene, **7** and **8** afford the corresponding bimetallic complexes **9** and **10**.



9, $M(CO)_n = Fe(CO)_4$ (yield 50%)
10, $M(CO)_n = Mo(CO)_5$ (yield 79%)

Complex **9** can also be obtained in 11% yield by reacting directly phosphine sulfide **3a** with $Fe_2(CO)_9$ in boiling toluene. The most significant ^1H NMR data of complexes **9** and **10** are given in Table I. The chemical shifts and the $^3J(H-H)$ coupling constants of the PhC*H* protons of these complexes fall within the same range as those of the corresponding protons in various authenticated [η^4-(*E,E*)-4-R-1-phenyl-1,3-butadienyl]iron tricarbonyl complexes. This result strongly favors a (*E,E*) structure for phosphines **5a** and its derivatives as suggested in the preceding paragraph.

As a conclusion we have shown that (*E*)-butadienylphosphines can act as η^2 or η^6 ligands and that two different metals can be complexed by such ligands. The Dreiding stereomodels of these compounds show, on the other hand, that the minimum distance between the two metals probably falls around 3.5 Å. This is a correct distance for bimetallic activation of small molecules.[28] Thus investigations of catalytic activity of such types of complexes would be of interest.

Experimental Section

NMR spectra [chemical shifts in ppm from Me_4Si for ^1H and from H_3PO_4 (external reference) for ^{31}P; δ positive for downfield shifts in both cases] were recorded for the proton on Perkin-Elmer R_{12} and R_{24} at 60 MHz and a Jeol P.S. 100 at 100 MHz and for the phosphorus on a Brucker WH-90 D.S. at 36.447 MHz; IR spectra were recorded on a Perkin-Elmer Model 457 and mass spectra on a MS30AEI spectrometer. Elemental analyses were performed by Service de Microanalyse de l'IRCHA (Vert-le-Petit).

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All reactions and manipulations were carried out under an argon atmosphere. Tetrahydrofuran (THF) was freshly distilled from sodium–benzophenone; chromatographic separations were performed on silica-gel columns (70-230 mesh MERCK). Metal carbonyls and $(\eta^5\text{-}C_5H_5)_2Ni$ were purchased from Strem Chemicals Inc.; $Fe(CO)_4THF$[25] and $Mo(CO)_5THF$[26] were prepared according to the literature.

Allyldiphenylphosphine Sulfide (1). Into a 2-L four-necked flask fitted with a mechanical stirrer, an addition funnel, and a water condenser topped with an argon inlet were placed 600 mL of THF and 8.2 g (1.18 g-atoms) of lithium wire which was cut in short pieces. Chlorodiphenylphosphine (132 g, 0.6 mol) in 200 mL of THF was added. The reaction mixture was stirred at ambient temperature for 20 h. The reaction was only mildly exothermic, and the color became deep red as the reaction proceeded. Allyl bromide (0.6 mol) was added, and the deep red color was discharged at the end of the addition. The solution was then hydrolyzed by the dropwise addition of deoxygenated water (200 mL). The clear yellow solution was decanted under argon, washed with water, dried, and evaporated to give a yellow viscous oil. Sulfuration was accomplished by heating this residue with sulfur (20 g) in benzene (100 mL) at reflux with stirring under argon for 30 min; crystallization from water and then from hexane gave phosphine sulfide **1**: 120 g (77.5%); mp 48 °C (lit.[27] mp 49–50 °C).

(*E*)-(4-Phenyl-4-hydroxy-1-butenyl)diphenylphosphine Sulfide (2a). Phosphine sulfide **1** (5 g, 1.93×10^{-2} mol) in THF (50 mL was added with stirring (15 min) to a solution of 1.49 M butyllithium in petroleum ether (16 mL) at −78 °C. The solution became deep orange-red; stirring and cooling were then continued while benzaldehyde (2.3 g, 2.16×10^{-2} mol) in THF (20 mL) was added slowly. The deep color was discharged. The solution was warmed to −20 °C; after 30 min, dilute hydrochloric acid was added. The solution was diluted with ether, washed with water, dried, and evaporated. The oily residue was chromatographed (eluant = benzene–ethyl acetate; 95:5; R_f = 0.25) and gave 4.38 g (62%) of **2a**: IR (film) $\nu(OH)$ 3390, $\nu(C{=}C)$ 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.66 (pseudo t, $^3J(H\text{–}H) = 6.8$ Hz, CH_2), 3.19 (br s, OH), 4.73 (t, $CH(OH)$) [AB system $\delta_A = 6.26$ ($^2J(H\text{–}P) = 24.0$, $^3J(H\text{–}H) = 16.5$ Hz), $\delta_B = 6.68$ ($^3J(H\text{–}P) = 22.5$ Hz)]; ^{31}P NMR δ +33.09.

(*E*)-(4,4-Diphenyl-4-hydroxy-1-butenyl)diphenylphosphine sulfide (2b) was prepared from phosphine sulfide **1** (2.5 g, 9.6×10^{-3} mol) and benzophenone (1.85 g, 1.01×10^{-2} mol) in essentially the same way as described above; the crude product was separated by chromatography (benzene–ethyl acetate, 95:5) giving 2.44 g (54.5%) of **2b**: mp 172 °C; IR ($CHCl_3$) $\nu(OH)$ 3450, $\nu(C{=}C)$ 1615, $\nu(P{=}S)$ 640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.26 (s, OH), 3.25 (m, CH_2), 6.19 (m, $=CH$); ^{31}P NMR δ +33.09.

(*E*)-(4-Methyl-4-hydroxy-1-pentenyl)diphenylphosphine Sulfide (2c) and Diphenyl(1-vinyl-2-methyl-2-hydroxypropyl)phosphine Sulfide (6). Metalation of the phosphine sulfide **1** (2.50 g, 9.6×10^{-3} mol) and reaction with acetone (0.6 g, 1.03×10^{-2} mol) as described above gave a crude product which was separated by chromatography (benzene–ethyl acetate, 95:5) giving 0.17 g (5.4%) of **6** as a white solid (R_f = 0.25) and **2c** (2 g, 63.2%) as a colorless oil (R_f = 0.1).

2c: IR (film) $\nu(OH)$ 3430, $\nu(C{=}C)$ 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (s, CH_3), 2.25 (d, $^3J(H\text{–}H) = 6$ Hz, CH_2), 3.1 (s, OH), 6.39 (m, $=CH$); ^{31}P NMR δ +32.9.

6: IR ($CHCl_3$) $\nu(OH)$ 3370, $\nu(C{=}C)$ 1630 cm^{-1}; ^1H NMR (CCl_4) δ 1.08 (s, CH_3), 1.1 (m, CH_3), 3.3 (t, $^3J(H\text{–}H) = 9$ Hz, $^2J(H\text{–}P) = 9$ Hz, CH), 4.2 (s, OH), 4.83 (m, $=CH_2$), 5.73 (m, $=CH$); ^{31}P NMR δ +38.78.

(*E*,*E*)-(4-Phenyl-1,3-butadienyl)diphenylphosphine Sulfide (3a). Dehydration of **2a** was accomplished by heating a solution of 9 g (2.47×10^{-2} mol) of **2a** and 0.1 g of *p*-toluenesulfonic acid in 100 mL of toluene at reflux with stirring under argon for 3.5 h; after evaporation of the solvent, the crude oil was chromatographed (eluant = benzene–ethyl acetate, 95:5), affording 7 g (84.3%) of **3a** (R_f = 0.4): mp 140.5 °C (from ether); IR ($CHCl_3$) $\nu(C{=}C)$ 1625, $\nu(P{=}S)$ 632, 602 cm^{-1}; ^{31}P NMR δ +33.89. Anal. Calcd for $C_{22}H_{19}PS$: C, 76.27; H, 5.52. Found: C, 76.07; H, 5.34.

(*E*)-(4,4-Diphenyl-1,3-butadienyl)diphenylphosphine sulfide (3b) was prepared from 1.79 g (3.85×10^{-3} mol) of **2b** in the same way as above; 1.5 g (92%) of **3b** was obtained: mp 149 °C (from ether); IR ($CHCl_3$) $\nu(C{=}C)$ 1600, $\nu(P{=}S)$ 638, 602 cm^{-1}; ^{31}P NMR δ +34.30. Anal. Calcd for $C_{28}H_{23}PS$: C, 79.59; H, 5.48. Found: C, 79.62; H, 5.26.

(*E*)-(4-Methyl-1,3-pentadienyl)diphenylphosphine sulfide (3c): mp 110 °C (from pentane–ether, 4:1); ^1H NMR ($CDCl_3$) δ 1.80 (s, CH_3), 6.5 (m, $=CH$); ^{31}P NMR δ +34.3. Anal. Calcd for $C_{18}H_{19}PS$: C, 72.45; H, 6.42. Found: C, 72.69; H, 6.40.

Preparation of Complexes $\eta^5\text{-}C_5H_5Ni(I)P(C_6H_5)_2R$. The complexes were prepared according to ref 21. Crude complexes were purified by chromatography. **4a** ($R = C_6H_5CH{=}CHCH{=}CH$) (eluant = hexane–benzene, 80:20; ρ = 70%): mp 176 °C (from ethanol–benzene); ^1H NMR (C_6D_6) δ 5.08 (s, C_5H_5), 7.08, 7.10, 7.65 (m, 19 H, $=CH$ and C_6H_5); ^{31}P NMR δ +30.63. Anal. Calcd for $C_{27}H_{24}INiP$: C, 57.39; H, 4.28; Ni, 10.39. Found: C, 57.97; H, 4.01; Ni, 10.01.

4b ($R = (C_6H_5)_2C{=}CHCH{=}CH$) (eluant = benzene; ρ = 55%): ^1H NMR (C_6D_6) δ 4.95 (s, C_5H_5), 6.95–7.55 (m, 23 H, $=CH$ and C_6H_5); ^{31}P NMR δ +32.18; mass spectrum (70 eV, 100 °C, ^{58}Ni), *m/e* 640 (0.5) [M], 390 (100) [$M - Ni(C_5H_5)I$].

4c ($R = (CH_3)_2C{=}CHCH{=}CH$) (eluant = hexane–benzene, 80:20; ρ = 65%): ^1H NMR (C_6D_6) δ 1.60 (s, CH_3), 5.0 (s, C_5H_5), 5.82–6.40 (m, 3 H, $=CH$); ^{31}P NMR δ +31.3; mass spectrum (70 eV, 80 °C, ^{58}Ni), *m/e* 516 (13) [M], 266 (100) [$M - Ni(C_5H_5)I$].

Preparation of Phosphines. A sample of 0.5 mL of $P(OCH_3)_3$ is added at room temperature to 3×10^{-3} mol of complexes **4a–c** dissolved in 20 mL of benzene. The red solution becomes rapidly green and then brown. After being stirred for 5 min, the mixture is evaporated and chromatographed on a short column.

(*E*,*E*)-(4-Phenyl-1,3-butadienyl)diphenylphosphine (5a) (eluant = hexane–benzene, 50:50; $R_f(C_6H_6)$ = 0.67): yield 50%; ^{31}P NMR (C_6D_6) δ −14.37. Benzyl(4-phenyl-1,3-butadienyl)diphenylphosphonium bromide: mp 104 °C; ^1H NMR ($CDCl_3$) δ 4.84 (br d, $^2J(H\text{–}P) = 14$, CH_2P).

(*E*)-4,4-(Diphenyl-1,3-butadienyl)diphenylphosphine (5b) (eluant = benzene; R_f = 0.72): yield 65%; ^{31}P NMR (C_6D_6) δ −14.57.

(*E*)-(4-Methyl-1,3-pentadienyl)diphenylphosphine (5c) (eluant = benzene; R_f = 0.7): yield 40%; ^1H NMR (C_6D_6) δ 1.43 (s, CH_3), 1.55 (s, CH_3), 5.7–6.8 (m, $=CH$); ^{31}P NMR δ −14.97.

[(*E*,*E*)-(4-Phenyl-1,3-butadienyl)diphenylphosphine]tetracarbonyliron (7). (a) From Phosphine 5a. A sample of 0.42 g (1.15×10^{-3} mol) of diiron nonacarbonyl was put in an Erlenmeyer flask with 150 mL of THF; 0.4 g (1.27×10^{-3} mol) of phosphine **5a** in 20 mL of the same solvent was added with stirring under a carbon monoxide flushing. The reaction mixture was stirred for 3 h at room temperature under 1 atm of carbon monoxide. The resulting orange solution was evaporated to give a brownish orange residue which was purified by chromatography (eluant = hexane–benzene, 60:40), affording 0.15 g (24%) of the expected complex (R_f = 0.7).

(b) From Phosphine Sulfide. **3a** (1.4 g, 4.0×10^{-3} mol), iron dodecacarbonyl (2 g, 3.9×10^{-3} mol), and toluene (100 mL), placed in a 250-mL Erlenmeyer flask, were heated at reflux with stirring under argon for 4 h. After cooling of the solution to room temperature, the black precipitate that formed was removed by filtration, the solvent evaporated, and the crude complex purified as above: yield 0.7 g (36.2%); mp 144 °C (from hexane); IR (Nujol) $\nu(CO)$ 2047 (s), 1975 (s), 1935 (vs) cm^{-1}; ^{31}P NMR (C_6D_6) δ +62.2; mass spectrum (70 eV, 125 °C); *m/e* 482 (5) [M], 454 (9) [M − CO], 426 (7) [M − 2CO], 398 (10) [M − 3CO], 370 (100) [M − 4CO], 319 (9) [M − 4CO − Fe]. Anal. Calcd for $C_{26}H_{19}FeO_4P$: C, 64.75; H, 3.94; Fe, 11.58. Found: C, 64.22; H, 3.97; Fe, 11.29.

[(*E*,*E*)-(4-Phenyl-1,3-butadienyl)diphenylphosphine]pentacarbonylmolybdenum (8). Phosphine **5a** (0.5 g, 1.59×10^{-3} mol) in 20 mL of THF was added to $Mo(CO)_5THF$ [from $Mo(CO)_6$ (0.65 g, 2.46×10^{-3} mol) irradiated for 1 h in 200 mL of THF] with stirring under argon; the reaction mixture was stirred for 1 h at room temperature. The solvent was then removed from the yellow solution. The yellow-brown oily residue was chromatographed (eluant = hexane–benzene, 80:20). The yield was 0.9 g (66.5%). IR (Nujol) $\nu(CO)$ 2070 (m), 1987 (m), 1947 (vs) cm^{-1}; ^{31}P NMR (C_6D_6) δ +25.05; mass spectrum (70 eV, 100 °C, ^{98}Mo); *m/e* 552 (13) [M], 524 (47) [M − CO], 496 (32) [M − 2CO], 468 (7) [M − 3CO], 440 (53) [M − 4CO], 412 (100) [M − 5CO], 314 (26) [M − 5CO − Mo]. Anal. Calcd for $C_{27}H_{19}MoO_5P$: C, 58.92; H, 3.48. Found: C, 58.73; H, 3.35.

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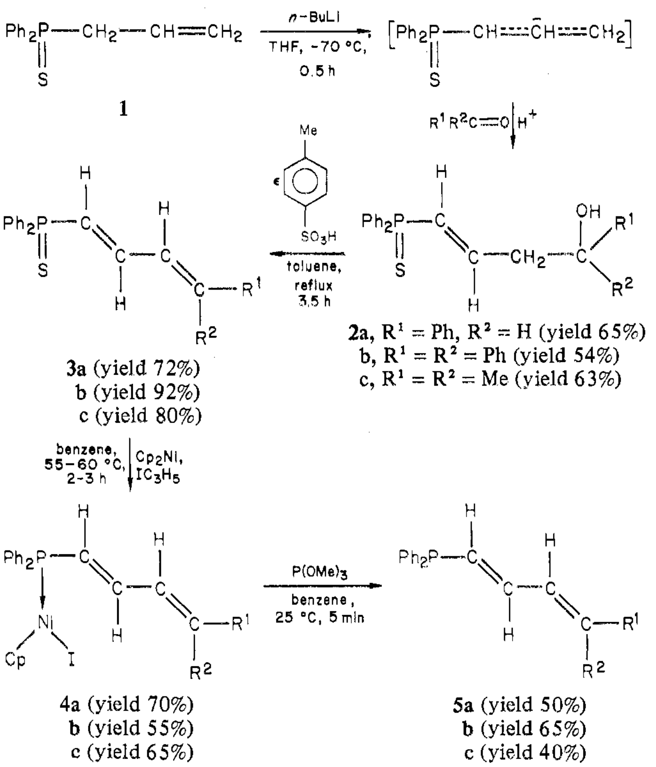
Scheme I. Synthesis of (*E*)-1,3-Butadienyldiphenylphosphines



[[[(*E*,*E*)-(η^4-4-Phenyl-1-(diphenylphosphinyl)-1,3-butadienyl)]tricarbonyliron]-*P*]tetracarbonyliron (9). **(a) From 7.** A mixture of complex **7** (0.3 g, 6.2 × 10^{-4} mol) and $Fe_3(CO)_{12}$ (0.3 g, 5.9 × 10^{-4} mol) in benzene (50 mL) was heated and stirred at 80 °C for 20 h in an argon atmosphere. After cooling of the solution to room temperature, the solvent was removed in vacuo. The oily residue chromatographed with hexane–benzene (60:40) gave first the starting complex **7** (0.1 g; $R_f = 0.75$) and then the orange complex **9** (0.2 g, 50%; $R_f = 0.4$).

(b) From Phosphine Sulfide. A mixture of **3a** (1 g, 3.18 × 10^{-3} mol) and $Fe_2(CO)_9$ (2 g, 5.49 × 10^{-3} mol) in toluene (50 mL) was heated and stirred at reflux in an argon atmosphere for 8 h. After cooling of the solution to room temperature, the black precipitate that formed was filtered and the solvent evaporated. The residue when chromatographed gave **7** (0.3 g, 20%) and **9** (0.2 g, 11%): IR (Nujol) 2055 (s), 2040 (m) 2010 (w), 1990 (s), 1965 (w), 1945 (s), 1905 (m) cm^{-1}; ^{31}P NMR δ +70.93; mass spectrum (70 eV, 80 °C), *m/e* 622 (13) [M], 594 (11) [M − CO], 566 (28) [M − 2CO], 538 (25) [M − 3CO], 510 (25) [M − 4CO], 482 (57) [M − 5CO], 454 (23) [M − 6CO], 426 (100) [M − 7CO], 370 (60) [M − 7CO − Fe], 314 (11) [M − 7CO − 2Fe].

[[[(*E*,*E*)-(η^4-4-Phenyl-1-(diphenylphosphinyl)-1,3-butadienyl)]tricarbonyliron]-*P*]pentacarbonylmolybdenum (10) was prepared from 0.9 g (1.63 × 10^{-3} mol) of **8** and 0.81 g (1.6 × 10^{-3} mol) of $Fe_3(CO)_{12}$ in the same way as above (procedure a). Chromatography (eluant = hexane–benzene, 90:10) gave first the starting complex **8** (0.1 g) and then complex **10**: 1 g (79%); $R_f = 0.35$; mp 102–103 °C (from pentane); IR (Nujol) 2070 (m), 2052 (m), 2000 (m), 1988 (m), 1951 (s, sh), 1945 (s) cm^{-1}; ^{31}P NMR (C_6D_6) δ +34.6; mass spectrum (70 eV, 100 °C, ^{98}Mo), *m/e* 692 (≃1) [M], 636 (≃1) [M − 2CO], 608 (3) [M − 3CO], 580 (2) [M − 4CO], 552 (2) [M −5CO], 524 (5) [M − 6CO], 496 (2) [M − 7CO], 468 (7) [M − 8CO], 412 (8) [M − Fe − 8CO], 370 (100) [M − Mo − 8CO], 314 (100) [M − Mo − Fe − 8CO].

Registry No. **1**, 10061-87-7; **2a**, 73210-27-2; **2b**, 73210-28-3; **2c**, 73210-29-4; **3a**, 73210-30-7; **3b**, 73210-31-8; **3c**, 73210-32-9; **4a**, 73210-37-4; **4b**, 73210-38-5; **4c**, 73210-39-6; **5a**, 73210-33-0; **5b**, 73210-34-1; **5c**, 73210-35-2; **6**, 73210-36-3; **7**, 73210-40-9; **8**, 73210-41-0; **9**, 73210-42-1; **10**, 73210-43-2; chlorodiphenylphosphine, 1079-66-9; allyl bromide, 106-95-6; benzaldehyde, 100-52-7; benzophenone, 119-61-9; acetone, 67-64-1; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8; $Mo(CO)_5THF$, 53248-43-4.

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Metal Phthalocyanine Complexes. 1. Synthesis and Properties of $[Ru(ClPC)(py)_2]\cdot 4py$ and $[Ru(ClPC)(PPh_3)_2]$

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A number of six-coordinate ruthenium(II) phthalocyanines have been prepared and are well characterized.[1-4] There has also been a report[5] of the preparation of several ruthenium(III) phthalocyanine complexes with the general formula [Ru(PC)ClL′], where L′ equals phthalonitrile or *o*-cyanobenzamide. When L′ is equal to pyridine, there are three or four additional pyridine molecules of crystallization, $[Ru(PC)Cl(py)]\cdot n py$ (n = 3 or 4). Elemental analyses and limited spectral and physical properties indicate, however, that the materials are not pure. Thus, we have attempted, by using the same procedure, to synthesize in a well-characterized form Ru(III) derivatives. It turns out, however, that we have synthesized Ru(II) complexes of the monochlorinated phthalocyanine macrocycle, $[Ru(ClPC)(py)_2]\cdot 4py$ and $[Ru(ClPC)(PPh_3)_2]$, in good yields (60–70%).

Experimental Section

All materials were obtained commercially and used without further purification. Infrared spectra were taken with a PE-457 spectrophotometer with the samples in a KBr disk. Electronic absorption spectra were taken with a Cary 14 spectrophotometer on benzene solutions. Magnetic susceptibility measurements on the solids at 20 °C were made with a Faraday balance at Vanderbilt University, while NMR spectra were taken with a 250-MHz spectrometer at Carnegie-Mellon University on saturated solutions of the complexes in deuterated dimethyl sulfoxide with Me_4Si as an internal standard. Thermal gravimetric measurements were made with a Perkin-Elmer TGA apparatus. The solid samples were placed in a N_2 stream (100 mL/min) and heated (10 °C/min) from ambient temperature to 900 °C, and the weight loss was recorded. Elemental analyses were done by Dornes U. Kolbe, Mulheim, West Germany.

$[Ru(ClPC)(py)_2]\cdot 4py$. An intimate mixture of the solids *o*-dicyanobenzene, 12.8 g (0.10 mol), and 2.6 g (0.01 mol) of $RuCl_3\cdot 3H_2O$ is made by grinding the materials thoroughly together in a mortar and pestle. The gray solid is heated in a 50-mL round-bottom flask fitted with an air condenser at 280 °C for 4 h. The resulting blue-black solid is cooled and transferred to a funnel. Extraction of the material with 5 × 50 mL of boiling distilled water removes excess *o*-dicyanobenzene. The remaining solid is transferred to a thimble which is placed in a Soxhlet extractor. Extraction with 150 mL of methanol is carried out for 48 h. At this point, the methanol solution in the extractor is light blue, while the flask contains a dark green solution. The methanol extract contains various hydrolysis products of *o*-dicyanobenzene and its trimer, 2,4,6-tris(*o*-cyanophenyl)-1,3,5-triazine. The solid is then extracted, in the same apparatus, with 150 mL of pyridine for 2 weeks. At the end of this time, the pyridine in the extractor is faintly blue while the pyridine in the flask is dark blue. The black residue left in the thimble amounts only to 0.3 g. The pyridine extract is evaporated to dryness in air to yield a red-violet solid; yield 7.2 g, 68% based on the ruthenium used. Anal. Calcd

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