

A 2,2'-Biphosphinine Dianion: Synthesis and Reactivity

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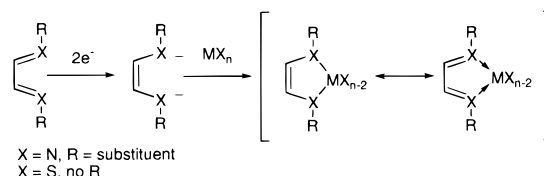
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The reduction of 4,4',5,5'-tetramethyl-2,2'-biphosphinine (tmbp) with excess Li, Na, or K affords the corresponding dianions. Reaction of these anions with metal halides gives (tmbp)-metal(0) complexes.

Phosphinines show specific electronic properties which markedly differ from those of classical tertiary phosphines and pyridines, their nitrogen analogues.¹ Their strong π -accepting ability can be exploited for the stabilization of several unusual homoleptic metal(0) complexes,² and recently, functionalized ligands were shown to play an interesting role in homogeneous catalysis.³ These results, as others, support the idea that the elaboration of sophisticated ligands including phosphinines as subunits is a worthy and exciting challenge in organophosphorus chemistry.⁴ With this aim, we synthesized in 1991 the first example of a 2,2'-biphosphinine.⁵ As expected, these new ligands revealed a better potential than their nitrogen counterparts for the stabilization of electron-rich and/or reduced transition metal complexes.^{1c,6} A significant illustration of this unique behavior was given by the electrochemical reduction of a homoleptic nickel complex into a dianionic species.^{2e} As part of a continuing program aimed at studying the coordination chemistry of these ligands, we were interested in developing a new efficient approach to metal(0) phosphinine complexes. Only two approaches to these types of complexes were known so far: reaction of the ligand with sophisticated zerovalent precursors (including metallic vapors)^{2b} or with metal

Scheme 1



halides in the presence of a reducing agent.^{2e,f} Unfortunately, the most rational and conventional approach, which would consist of reducing phosphinine complexes of metals in high oxidation states, is not achievable since they exhibit poor stability.⁷ As previously observed in sulfur (dithiolenes)⁸ and nitrogen (1,4-diazadienes⁹ and bipyridine¹⁰) chemistry, the use of reduced ligands turns out to be a powerful method for the synthesis of metal complexes having various oxidation states (Scheme 1).

Phosphinine monoanion radicals, dianions, and even trianions (only when the ring bears phenyl groups), which are obtained via the reaction with alkali metals, exist, but to the best of our knowledge, no report deals with their use in the preparation of transition-metal complexes.¹¹ In this article, we describe our investigations on the synthesis and the reactivity of 2,2'-biphosphinine dianions.

All our experiments were carried out with the readily available 4,4',5,5'-tetramethyl-2,2'-biphosphinine (tmbp; **1**). The reduction which occurs in THF or in DME at room temperature using Li, Na, or K shows after 20 min an intense deep purple color. The absence of a ³¹P NMR signal at this stage suggests that the species formed is the paramagnetic monoanion radical **2**. After 2 h the

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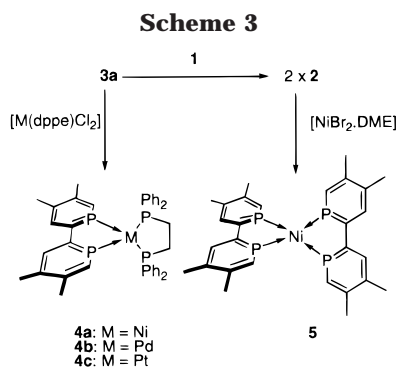
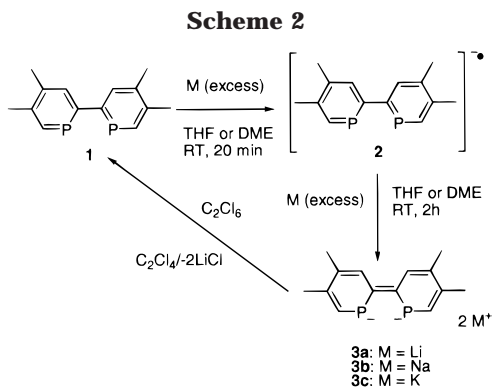
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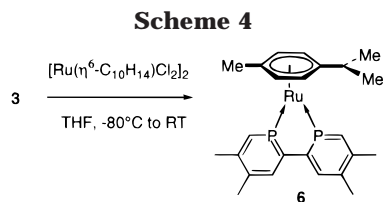
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color definitely turned dark green, indicating the end of the reaction. The reappearance of a ^{31}P NMR signal indicates that this new species is the diamagnetic dianion **3**, which turns out to be highly sensitive toward moisture and oxygen. Chemical evidence supporting the formation of **3** was given by its reaction with a stoichiometric equivalent of hexachloroethane, which gives back biphosphinine **1**, thus showing that the structure of the biphosphinine has been preserved (Scheme 2).

The ^{31}P NMR spectrum of each dianion **3** consists of a very broad peak at high field (between -5 and -15 ppm depending on the metal used). These differences, which have already been observed and discussed for other phosphorus anions such as Ph_2PM (M = Li, Na, K), very likely reflect the degree of solvation of the salt.¹² These chemical shifts, which strongly differ from that of **1** ($\delta(\text{THF})$: 182.0 ppm), cannot be compared to those of similar species, since ^{31}P NMR data of phosphinine dianions are still unknown. Interestingly, the ^1H NMR spectrum of **3** at 255 K reveals the presence of two protons at 6.68 and 7.00 ppm, in the usual range of vinylic protons, which were respectively ascribed to $\text{H}_{6,6'}$ and $\text{H}_{3,3'}$. The fact that these two signals are significantly shielded compared to that of **1** (7.83 ($\text{H}_{3,3'}$) and 8.37 ($\text{H}_{6,6'}$) ppm) indicates the loss of aromaticity in both phosphinine subunits and the localization of the double bonds. On the basis of these observations, we propose the structure for dianions **3** given in Scheme 2. In a sense, **3** can be regarded as the cyclic derivative analogue of *cis*-bis(1-R-lithiophosphino)ethene anions, which have been synthesized from the reaction of 1,2-dihydro-1,2-diphosphines with alkali metals.¹³ Our first



experiments were directed toward the synthesis of known complexes of **1**. The reaction of **3** with 1 equiv of $[\text{Ni}(\text{dppe})\text{Cl}_2]$ cleanly yields $[\text{Ni}(\text{dppe})(\text{tmbp})]$ (**4a**), which had already been obtained through the reaction of biphosphinine **1** with $[\text{Ni}(\text{dppe})\text{Cl}_2]$ in the presence of LiBET_3H and *trans*-stilbene.¹⁴ In a similar manner, we also prepared the previously unknown $[\text{Pd}(\text{dppe})(\text{tmbp})]$ (**4b**) and $[\text{Pt}(\text{dppe})(\text{tmbp})]$ (**4c**) analogues, which were isolated in very good yields. To assess whether mono-anion radical species such as **2** could also be used as a source of metal(0) complexes, we reinvestigated the synthesis of $[\text{Ni}(\text{tmbp})_2]$ (**5**).^{2e} As stated above, mono-anion **2** is transiently formed during the reduction of **1**. We have found that it can be conveniently obtained by comproportionation of dianion **3** with 1 equiv of biphosphinine **1** at low temperature, as depicted in Scheme 4. As expected, the reaction of 2 equiv of **2** with the $[\text{NiBr}_2 \cdot (\text{DME})]$ precursor yields the $[\text{Ni}(\text{tmbp})_2]$ complex (Scheme 3).

These encouraging results prompted us to investigate the preparation of a new species, the $[\text{Ru}(\eta^6\text{-C}_{10}\text{H}_{14})(\text{tmbp})]$ complex **6**, which is the first example of a Ru(0) biphosphinine complex. Some years ago, we studied the in situ chemical reduction of the cationic $[\text{Ru}(\eta^6\text{-C}_{10}\text{H}_{14})(\text{tmbp})\text{Cl}][\text{Cl}]$ precursor, which turned out to be too sensitive toward hydrolysis to be isolated under satisfactory conditions and led to the isolation of several unidentified species. We ascribed this failure to the difficulty of controlling a stoichiometric reduction process. The use of dianion **3** proves to be a convenient and powerful approach to this type of complex. The reaction of 1 equiv of **3** with 0.5 equiv of $[\text{Ru}(\eta^6\text{-C}_{10}\text{H}_{14})(\text{tmbp})\text{Cl}_2]_2$ dimer cleanly yields complex **6** as red crystals after extraction with toluene (Scheme 4).

Unlike other known $[\text{Ru}(\eta^6\text{-C}_{10}\text{H}_{14})(\text{R}_3\text{P})_2]$ complexes, which are highly oxygen sensitive species,¹⁵ we found that **5** can be handled in air for appreciable periods without any difficulties. We think this stability results from the strong π -accepting ability of biphosphinine, which reduces the electron density at the Ru center. All NMR (^{31}P , ^1H , ^{13}C) data and combustion analysis support the formulation of **6**. Definitive evidence was provided by a X-ray crystal structure analysis. An ORTEP drawing of **6** is presented in Figure 1, and significant bond lengths and angles are quoted below.

The first interesting remark concerns the overall geometry of the complex. The biphosphinine ligand ($\text{P}_2\text{C}_5\text{C}_6\text{P}_3$ plane) is nearly perpendicular ($\theta = 85.7^\circ$) to the plane defined by the aromatic ring ($\text{C}_{15}\text{-C}_{20}$). This value compares with that reported for the $[\text{Fe}(\eta^6\text{-$

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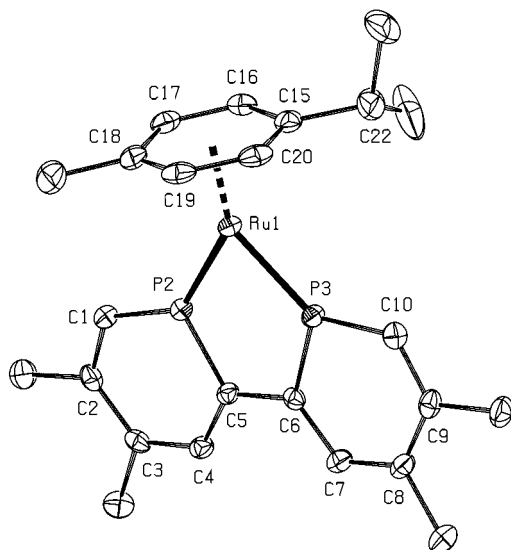
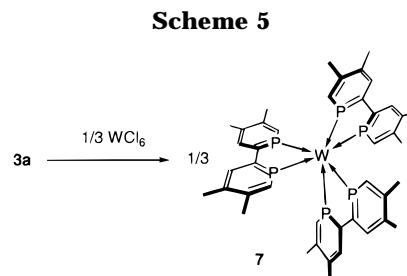


Figure 1. ORTEP drawing of one molecule of **6**. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. The crystallographic labeling is arbitrary and different from the numbering used for assignments of the NMR spectra. Selected bond distances (Å): Ru1–P2, 2.2080(7); Ru1–P3, 2.233(3); Ru1–C15, 2.249(3); Ru1–C16, 2.241(3); Ru1–C17, 2.236(3); Ru1–C18, 2.247(3); Ru1–C19, 2.255(3); P2–C1, 1.727(3); P2–C5, 1.749(3); P3–C10, 1.728(3); P3–C6, 1.751(3); C1–C2, 1.389(4); C2–C3, 1.411(4); C3–C4, 1.396(4); C4–C5, 1.399(4); C5–C6, 1.447(4); C6–C7, 1.396(4); C7–C8, 1.392(4); C8–C9, 1.410(4); C9–C10, 1.382(4); Ru–centroid, 1.742(2). Selected bond angles (deg): P2–Ru–P3, 77.82(3); C5–P2–C1, 103.1(1); C10–P3–C6, 103.1(1); P2–C1–C2, 124.6(2); C1–C2–C3, 122.9(2); C2–C3–C4, 122.2(2); C3–C4–C5, 125.8(2); C4–C5–P2, 121.1(4); P2–C5–C6, 112.2(2); C4–C5–C6, 126.5(2).

toluene)(bpy)] complex reported by Klabunde et al.¹⁶ Interestingly, the arene unit turns out to be perfectly planar (deviations out of the plane from 0.001 to 0.01(3) Å), thus showing that an important electronic transfer from the metal to the π^* system of the ligand occurs. Indeed, calculations performed on π -arene ML_2 complexes have shown that a planar geometry is a strong sign of significant metal-to-ligand electron delocalization.¹⁷ In line with this observation, the geometry of the biphosphinine is slightly modified when compared to that of the free ligand. In each unit, the two P–C bond lengths are markedly different, the internal bonds (P2–C5 = 1.749(3) and P3–C6 = 1.751(3) Å) being longer than the externals (P2–C1 = 1.727(3) and P3–C10 = 1.728(3) Å). Also noteworthy is the C5–C6 bridge distance, which is rather short (1.447(4) vs 1.490(8) Å in *cis*-**1**). As we proposed above, these data confirm that there is a sizable electronic delocalization within the RuPCCP unit, since the π^* LUMO of biphosphinine is bonding between the two subunits and antibonding between phosphorus and carbon. A similar statement has been stressed for Klabunde's bipyridine complex and for the homoleptic $[W(\text{tmbp})_3]$ complex.^{2f} Apart from these distortions which only concern the PCCP unit, distances within the rings are quite normal and no disruption of the aromaticity is observed.

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So far, we only studied the reduction of dihalide salts of metals without observing redox processes leading back to **1**. To enlarge the scope of this study, we extended our experiments to the synthesis of the homoleptic $[W(\text{tmbp})_3]^{2f}$ complex **7**, whose formation requires six successive reduction steps. The reaction of 3 equiv of dianion **3** with WCl_6 in THF at -80°C affords complex **7** and ligand **1** in a 95:5 ratio, respectively. After extraction of reformed biphosphinine **1** with hexanes and elimination of LiCl salts, complex **7** was isolated in 75% yield as red crystals (Scheme 5).

This last result clearly shows that redox processes are not favored, even when several reduction steps are involved, and thus constitutes an encouraging sign for further studies. We are currently exploring the chemistry of dianion **3** toward other metallic centers having various oxidation states, and preliminary results show that this approach should be particularly convenient for the synthesis of negatively charged and excessively electron rich biphosphinine metal complexes. We will report on these studies in due course.

Experimental Section

All reactions were routinely performed under an inert gas (nitrogen or argon) using Schlenk techniques and dry, oxygen-free solvents. Dry toluene, hexane, THF, and DME were obtained by distillation from sodium/benzophenone, and dry CH_2Cl_2 was obtained by distillation from P_2O_5 . Dry Celite was used for filtration. NMR spectra were recorded on a Bruker AC-200 SY operating at 200.12 MHz for 1H , 50.32 MHz for ^{13}C , and 81.91 MHz for ^{31}P ; for dianion **3a**, 1H and ^{13}C NMR spectra were also recorded on a Bruker AMX-400 operating at 100.62 MHz for 1H and 400.14 MHz for ^{13}C . Solvent peaks are used as an internal reference relative to Me_4Si at 0 ppm for 1H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. List of abbreviations used: s, singlet; d, doublet; t, triplet; q, quadruplet; p, pseudo; b, broad. Elemental analyses were recorded at the "Service d'analyse du CNRS", Gif-sur Yvette, France. Biphosphinine **1**,^{5b} $[M(\text{dppe})Cl_2]$ ($M = Ni,^{18} Pd,^{19} Pt^{20}$), $[NiBr_2]\cdot\text{DME}$,²¹ and $[Ru(\eta^6\text{-C}_{10}\text{H}_{14})Cl_2]_2$ ²² were prepared according to reported procedures.

General Procedure for the Preparation of 4,4',5,5'-Tetramethyl-2,2'-biphosphinine Dianions 3a–c. Biphosphinine **1** (24 mg, 0.1 mmol) was dissolved in dry THF (or DME) (2 mL), and the resulting solution was thoroughly degassed thrice by freezing and thawing under static vacuum. Li, Na, or K (excess) was added to the reaction mixture under a stream of argon, and the reaction mixture was stirred at room temperature. The reaction starts immediately with Na

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and K. With Li, the surface of the metal may need to be activated by stripping with a spatula. The color slowly evolved from yellow to deep purple and then to dark green, indicating the end of the reaction (2 h in general). Dianions **3a–c** are highly oxygen sensitive and ^{31}P NMR samples were prepared using a glovebox. Solutions of **3a–c** can be kept at room temperature for days without apparent decomposition. A solution of **3a** in THF- d_8 was sealed in a NMR tube in order to measure all NMR spectra.

3a: ^{31}P NMR ($\text{C}_4\text{D}_8\text{O}$, 255 K) δ -13.90; ^1H NMR ($\text{C}_4\text{D}_8\text{O}$, 255 K) δ 1.90 (s, 6H, 2 \times Me), 1.93 (s, 6H, 2 \times Me), 6.69 (pt, AA'XX', 2H, $^2J(\text{H}-\text{P}) = 38.50$ Hz, $\text{H}_{6,6'}$), 7.01 (s, AA'XX', $\text{H}_{3,3'}$); ^{13}C NMR ($\text{C}_4\text{D}_8\text{O}$, 255 K) δ 23.5 (s, Me), 24.40 (s, Me), 116.35 (bs, AXX', $\text{C}_{2,2'}$ or $\text{C}_{4,4'}$ or $\text{C}_{5,5'}$), 116.80 (bs, AXX', $\text{C}_{2,2'}$ or $\text{C}_{4,4'}$ or $\text{C}_{5,5'}$), 122.30 (bs, AXX', $\text{C}_{3,3'}$), 124.05 (bs, AXX', $\text{C}_{2,2'}$ or $\text{C}_{4,4'}$ or $\text{C}_{5,5'}$), 140.75 (bs, AXX', $\text{C}_{6,6'}$). **3b:** ^{31}P NMR ($\text{C}_4\text{H}_8\text{O}$) δ -6.10. **3c:** ^{31}P NMR ($\text{C}_4\text{H}_8\text{O}$) δ -4.20.

General Procedure for the Preparation of $[\text{M}^0(\text{dppe})-(4,4',5,5'\text{-tetramethyl-2',2'-biphosphinine})]$ (4a**, **M** = **Ni**; **4b**, **M** = **Pd**; **4c**, **M** = **Pt**).** The complexes $[\text{M}(\text{dppe})\text{Cl}_2]$ (0.1 mmol) were added at -80 $^\circ\text{C}$ to a solution of dianion **3a** in THF prepared as previously described. After 5 min of stirring at -80 $^\circ\text{C}$, the resulting mixture was slowly warmed to room temperature and then stirred for 30 min. After evaporation of THF, dry toluene (10 mL) was added and the solution obtained was filtered through a pad of Celite under a nitrogen atmosphere. After evaporation of toluene, complexes **4a–c** were recovered as moisture- and oxygen-sensitive red-orange powders. Yield: 80%. The compounds **4b,c** were too sensitive to give satisfactory elementary analyses. For characterizations of **4a**, see ref 13.

4b: ^{31}P NMR (C_6D_6) δ 176.60 (t, $^2J(\text{P}-\text{P}) = 23.2$ Hz, $\text{C}_{14}\text{H}_{16}\text{P}_2$), 38.5 (t, dppe); ^1H NMR (C_6D_6) δ 1.55–2.24 (m, 4H, CH_2), 2.24 (s, 6H, 2 \times Me), 2.27 (d, $J(\text{H}-\text{P}) = 2.15$ Hz, 6H, 2 \times Me), 6.99–7.07 (m, 12H, C_6H_5), 7.65–7.75 (m, 10H, CH of C_6H_5 and $\text{H}_{3,3'}$ of $\text{C}_{14}\text{H}_{16}\text{P}_2$), 8.64 (pt, AA'XX', 2H, $^2J(\text{H}-\text{P}) = 9.80$ Hz, $\text{H}_{6,6'}$ of $\text{C}_{14}\text{H}_{16}\text{P}_2$); ^{13}C NMR (C_6D_6) δ 23.25 (s, Me), 24.65 (s, Me), 29.95 (ptt, AXX'Y₂, $\sum J(\text{C}-\text{P}) = 42.73$ Hz, $^3J(\text{C}-\text{P}) = 5.00$ Hz, 2 \times CH_2), 129.00–129.90 (CH of C_6H_5 masked by C_6D_6), 130.45 (ptt, AXX'Y₂, $\sum J(\text{C}-\text{P}) = 18.30$ Hz, $^4J(\text{C}-\text{P}) = 3.05$ Hz, $\text{C}_{3,3'}$ of $\text{C}_{14}\text{H}_{16}\text{P}_2$), 131.65 (s, CH of C_6H_5), 133.95 (d, $J(\text{C}-\text{P}) = 16.85$ Hz, CH of C_6H_5), 139.00 (m, AXX'Y₂, $\text{C}_{6,6'}$ of $\text{C}_{14}\text{H}_{16}\text{P}_2$), 141.55 (AXX', $\sum J(\text{C}-\text{P}) = 13.74$ Hz, $\text{C}_{4,4'}$ or $\text{C}_{5,5'}$ of $\text{C}_{14}\text{H}_{16}\text{P}_2$), 142.60 (AXX', $\sum J(\text{C}-\text{P}) = 12.20$ Hz, $\text{C}_{4,4'}$ or $\text{C}_{5,5'}$ of $\text{C}_{14}\text{H}_{16}\text{P}_2$), 155.50 (m, AXX'Y₂, $\text{C}_{2,2'}$ of $\text{C}_{14}\text{H}_{16}\text{P}_2$).

4c: ^{31}P NMR (C_6D_6) δ 152.45 (t, $^2J(\text{P}-\text{P}) = 63.80$ Hz, $^1J(\text{P}-^{195}\text{Pt}) = 3045.00$ Hz, $\text{C}_{14}\text{H}_{16}\text{P}_2$), 43.40 (t, $^1J(\text{P}-^{195}\text{Pt}) = 3799.95$ Hz, dppe); ^1H NMR (C_6D_6) δ 1.54–2.24 (m, 4H, CH_2), 2.27 (s, 6H, 2 \times Me), 2.35 (d, $J(\text{H}-\text{P}) = 2.15$ Hz, 6H, 2 \times Me), 7.01–7.05 (m, 12H, C_6H_5), 7.61–7.9 (m, 10H, CH of C_6H_5), 8.43–8.58 (m, 2H, $\text{H}_{3,3'}$ of $\text{C}_{14}\text{H}_{16}\text{P}_2$), 8.82 (pt, AA'XX', 2H, $^2J(\text{H}-\text{P}) = 13.50$ Hz, $\text{H}_{6,6'}$ of $\text{C}_{14}\text{H}_{16}\text{P}_2$); ^{13}C NMR (C_6D_6) δ 23.30 (s, Me), 25.25 (pt, Me), 30.90 (ps, 2 \times CH_2), 129.00–130.1 (CH of C_6H_5 masked by C_6D_6), 133.80 (s, CH of C_6H_5), 134.00 (pt, AXX', $\sum J(\text{C}-\text{P}) = 14.95$ Hz, $\text{C}_{3,3'}$ of $\text{C}_{14}\text{H}_{16}\text{P}_2$), 137.00 (m, $\text{C}_{6,6'}$ of $\text{C}_{14}\text{H}_{16}\text{P}_2$), 139.15 (m, $\text{C}_{4,4'}$ or $\text{C}_{5,5'}$ of $\text{C}_{14}\text{H}_{16}\text{P}_2$), 143.80 (pt, AXX', $\sum J(\text{C}-\text{P}) = 12.60$ Hz, $\text{C}_{4,4'}$ or $\text{C}_{5,5'}$ of $\text{C}_{14}\text{H}_{16}\text{P}_2$), 148.75 (m, AXX'Y₂, $\text{C}_{2,2'}$ of $\text{C}_{14}\text{H}_{16}\text{P}_2$).

Synthesis of Bis(4,4',5,5'-tetramethyl-2',2'-biphosphinine)nickel(0) (5). Biphosphinine **1** (24 mg, 0.1 mmol) was added at -80 $^\circ\text{C}$ to a THF solution of dianion **3a** (24 mg, 0.1 mmol) prepared as previously described. The color of the mixture rapidly changed from dark green to deep purple. After 5 min of stirring, the resulting mixture was warmed to room temperature and then stirred for an additional 10 min. The reaction with $[\text{NiBr}_2\cdot\text{DME}]$ (31 mg, 0.1 mmol) was carried out at -80 $^\circ\text{C}$. The solution turned immediately dark red. After 5 min of stirring, the reaction mixture was warmed to room temperature. The solvent was evaporated, and complex **5** was extracted with dichloromethane (2 \times 5 mL). ^{31}P NMR showed two resonances corresponding to complex **5** and biphosphinine

Table 1. Crystallographic Data and Experimental Parameters for the Structure of 6

mol formula	$\text{C}_{24}\text{H}_{30}\text{P}_2\text{Ru}$
mol wt	481.49
cryst descriptn (habit/size (mm))	dark red needles/ 0.10 \times 0.12 \times 0.16
cryst syst	monoclinic
space group	$C2/c$
<i>a</i> (Å)	19.2260(5)
<i>b</i> (Å)	20.2100(5)
<i>c</i> (Å)	12.2910(2)
β (deg)	111.0550(13)
<i>V</i> (Å ³)	4456.91(18)
<i>Z</i>	8
<i>d</i> (g/cm ³)	1.435
<i>F</i> (000)	1984
μ (cm ⁻¹)	0.853
<i>T</i> (K)	150.0(1)
max θ (deg)	26.36
<i>hkl</i> ranges	0–24; 0–25; –15 to +14
no. of rflns measd	9386
no. of indep rflns	4558
no. of rflns used	3869
refinement type	F^2 ; full matrix
hydrogen atoms	mixed
no. of params refined	251
rfln/param ratio	15
wR2	0.0923
R1	0.0297
criterion	$I > 2\sigma(I)$
GOF	1.12
diff peak/hole (e Å ⁻³)	0.46 (0.13)/–0.60 (0.13)

1 in a 3:1 ratio. Washing with hexanes (2 \times 5 mL) gave pure complex **5**. Yield: 44 mg (80%). For characterizations, see ref 2e.

Synthesis of (η^6 -Cymene)(4,4',5,5'-tetramethyl-2',2'-biphosphinine)ruthenium(0) 6. The dimer $[\text{Ru}(\eta^6\text{-C}_{10}\text{H}_{14})\text{Cl}_2]_2$ (30.6 mg, 0.05 mmol) was added to a solution of dianion **3a** (49 mg, 2 mmol), prepared as described above in THF, at -80 $^\circ\text{C}$. The resulting red solution was kept at this temperature with stirring for 10 min and then slowly warmed to room temperature. After 20 min of stirring, a ^{31}P NMR control indicated that the reaction was complete. The solvent was then evaporated, and 40 mL of dry toluene was added. The resulting red mixture was stirred for an additional 20 min and then filtered under a nitrogen atmosphere. After evaporation of toluene, complex **6** was recovered as a red powder which is not particularly air-sensitive and can be weighed in air. Further purification can be achieved by crystallizing **6** in hexanes or pentane at room temperature. Yield: 37 mg (80%).

^{31}P NMR (C_6D_6): δ 200.5. ^1H NMR (C_6D_6): δ 1.13 (d, 6H, $^3J(\text{H}-\text{H}) = 6.87$ Hz, Me of isopropyl), 2.06 (s, 3H, Me of $\text{C}_{10}\text{H}_{14}$), 2.29 (s, 6H, Me of $\text{C}_{14}\text{H}_{16}\text{P}_2$), 2.41 (s, 6H, Me of $\text{C}_{14}\text{H}_{16}\text{P}_2$), 2.48 (septuplet, 1H, $^3J(\text{H}-\text{H}) = 6.87$ Hz, CH of isopropyl), 5.36 (m, 4H, CH of $\text{C}_{10}\text{H}_{14}$), 8.02 (AA'XX', 2H, $\sum J(\text{H}-\text{P}) = 25.63$ Hz, $\text{H}_{3,3'}$ or $\text{H}_{6,6'}$), 8.46 (AA'XX', 2H, $\sum J(\text{H}-\text{P}) = 20.49$ Hz, $\text{H}_{3,3'}$ or $\text{H}_{6,6'}$). ^{13}C NMR (C_6D_6): δ 21.40 (s, Me of $\text{C}_{10}\text{H}_{14}$), 22.50 (s, Me of isopropyl), 24.30 (d, $J(\text{C}-\text{P}) = 2.70$ Hz, Me of $\text{C}_{14}\text{H}_{16}\text{P}_2$), 24.60 (t, $J(\text{C}-\text{P}) = 4.70$ Hz, Me of $\text{C}_{14}\text{H}_{16}\text{P}_2$), 33.00 (s, CH of isopropyl), 80.60 (t, $^2J(\text{C}-\text{P}) = 2.40$ Hz, CH of $\text{C}_{10}\text{H}_{14}$), 82.80 (t, $^2J(\text{C}-\text{P}) = 2.40$ Hz, CH of $\text{C}_{10}\text{H}_{14}$), 95.05 (t, $^2J(\text{C}-\text{P}) = 2.50$ Hz, C_{ipso} of $\text{C}_{10}\text{H}_{14}$), 107.90 (t, $^2J(\text{C}-\text{P}) = 2.50$ Hz, C_{ipso} of $\text{C}_{10}\text{H}_{14}$), 129.00 (t, AXX', $\sum J(\text{C}-\text{P}) = 14.70$ Hz, C_4 or C_5), 130.00 (C_4 or C_5 masked by C_6D_6), 134.05 (t, AXX', $\sum J(\text{C}-\text{P}) = 8.40$ Hz, C_3), 142.05 (t, AXX', $\sum J(\text{C}-\text{P}) = 81.20$ Hz, $\text{C}_{2,2'}$), 142.25 (t, AXX', $\sum J(\text{C}-\text{P}) = 11.40$ Hz, $\text{C}_{6,6'}$). Anal. Calcd for $\text{RuC}_{24}\text{H}_{30}\text{P}_2$: C, 59.87; H, 6.28. Found: C, 59.60; H, 6.10.

Synthesis of Tris(4,4',5,5'-tetramethyl-2',2'-biphosphinine)tungsten(0) 7. WCl_6 (27 mg, 0.67 mmol) was added to a solution of **3a** (0.05 g, 0.2 mmol) at -80 $^\circ\text{C}$ in THF (5 mL). The reaction mixture was stirred at this temperature for 10 min and then slowly warmed to room temperature. After 20 min of stirring, the solvent was evaporated and complex **7** was

extracted with dichloromethane (20 mL). After evaporation, **7** was recovered as a deep purple powder. Yield: 46 mg (75%). For characterization, see ref 2f.

X-ray Structure Determination. Crystals suitable for X-ray diffraction were obtained from a hexane solution of complex **6**. Data were collected on a Nonius Kappa CCD diffractometer using an Mo K α ($\lambda = 0.71070 \text{ \AA}$) X-ray source and a graphite monochromator. The crystal structures were solved using maXus.²³ While initial refinement was performed with the latter, final least squares was conducted with Shelxl97.²⁴ Illustrations were made using Platon.²⁵ Crystal data are assembled in Table 1.

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Supporting Information Available: Listings of atomic coordinates, including H atoms and equivalent isotropic displacement parameters, bond lengths, and bond angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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