Stable Organopalladium(II) and Organoruthenium(II) Complexes with Spin-Labeled Phosphine Ligands

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Palladium(II) and ruthenium(II) complexes containing aminoxyl radical-substituted triphenylphosphine ligands are reported. The novel spin-labeled phosphine ligands [(*p*-(4,4,5,5,-tetramethylimidazolinyl-1-oxyl-3-oxide)phenyl)diphenylphosphine] (**1**) and [(*p*-(*N*-oxyl-*tert*-butylamino-2-)phenyl)diphenylphosphine] (**2**) react with $PdCl_2$ to yield *trans*-Pd[**1**]$_2$Cl$_2$ and *trans*-Pd[**2**]$_2$Cl$_2$ (complexes **3** and **4,** respectively), which show exchange-coupled EPR spectra. This through-space, intramolecular coupling provides a method of determining the number of radical phosphines coordinated to the Pd(II) center. Systems with only one coordinated phosphine show EPR spectra typical of the ligand. Phosphine **2** reacts with [(η^3-C_3H_5)PdCl]$_2$ and [(η^6-*p*-cymene)RuCl$_2$]$_2$ to form the mononuclear metal phosphine adducts (η^3-C_3H_5)Pd[**2**]Cl (**5**) and (η^6-*p*-cymene)Ru[**2**]Cl$_2$ (**6**). All complexes show broad, shifted ^{1}H NMR spectra, and magnetic susceptibility measurements confirm the presence of one (complexes **5**, **6**) or two (complexes **3**, **4**) radicals per complex accordingly. The X-ray crystal structures of Pd[**2**]$_2$Cl$_2$ and (η^3-C_3H_5)Pd[**2**]Cl are also reported. Complexes **5** and **6** are unusual examples of stable organometallic systems with peripheral free radicals, i.e., spin-labeled organometallics.

Introduction

The spin-labeling technique, which involves the incorporation of a stable free radical into a larger, complex system in a noninvasive fashion, has found great utility in macromolecular and biological chemistry.[1,2] Stable *N*-aminoxyl and nitronyl nitroxide radicals are featured strongly in these studies.[3,4] Generally, EPR spectroscopy is used to probe the local environment of the radical. The high sensitivity of EPR spectroscopy allows these investigations to proceed at very low concentrations of complex.[5] The use of spin-labeling has proven important for unraveling such issues as cholesterol interactions in biological membranes and peptide structures in solution.[4,6,7]

In contrast, the use of spin-labeling in organometallic chemistry is far less common. Although nitroxide radicals are known to interact directly with metal centers via the N−O group as a weak ligand,[8−10] in these systems the radical groups are actively involved with the metal center and hence cannot be termed “spin-labeled” complexes. One notable example of a simple route for addition of a remote spin label to organometallic systems is the oxidative addition of alkyl bromides (R−Br) to (bipy)PtMe$_2$, where the alkyl R-group contains a pendant TEMPO radical.[11] This method of integration of a spin label into organometallics, while clearly facile, is specific to metals that can undergo oxidative addition reactions. On the other hand, phosphines are ubiquitous in organometallic chemistry and especially important in catalysis.[12] The use of spin-labeled phosphines would thus provide a particularly simple method to introduce a spin label into a wide range of organometallic systems. In this paper we present novel triphenylphosphine ligands that have been spin-labeled with stable aminoxyl and nitronyl nitroxide radicals and illustrate their stability when bound to catalytically important organometallic palladium(II) and ruthenium(II) complexes.

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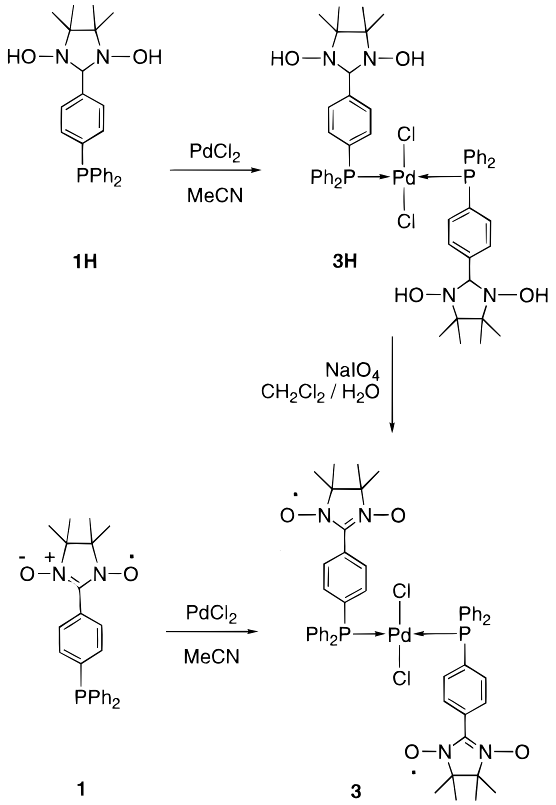
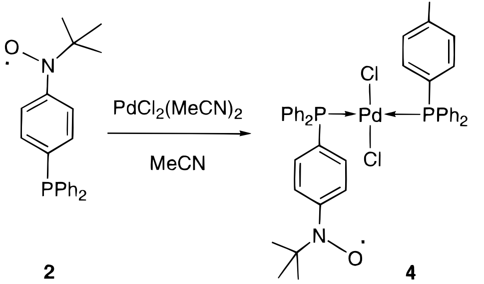
Scheme 1



Results and Discussion

Synthesis and Characterization of Spin-Labeled *trans*-$PdCl_2(PPh_3)_2$ Complexes. The synthesis of phosphines **1**[13,14] and **2**[15,16] has been previously described. Reaction of the radical precursor **1H** with $PdCl_2(MeCN)_2$ and subsequent *in situ* oxidation of the product **3H** with $NaIO_4$ gave the final radical-containing *trans*-Pd[**1**]$_2$Cl$_2$ complex **3** in good yield (Scheme 1) as a green solid. The same product could be obtained directly by reaction of $PdCl_2(MeCN)_2$ with phosphine **1** but in lower overall yield.

Similarly, the reaction of phosphine **2** with $PdCl_2(MeCN)_2$ gave the corresponding orange complex **4** in moderate yield (eq 1). The products are air and moisture stable and, more important, are stable with respect to decomposition of the radical.



(1)

^{1}H NMR spectra are observable for the complexes, but due to the presence of the unpaired electrons, the resonances are broadened and shifted relative to their diamagnetic counterparts and all coupling information is lost.[17] The proton resonances of the radical-substituted phenyl group could not be observed due to delocalization of the unpaired electron into this fragment. The phenyl protons of the unsubstituted rings are found at $\delta = 7.25$ and 7.6 ppm in **3** and at $\delta = 8.6$, 7.6, and 7.4 ppm in **4**. The methyl groups adjacent to the nitroxide moiety are visible only in **4** at $\delta = -1.55$ ppm as a very broad signal.

The variable-temperature magnetic susceptibility of **3** and **4** was measured on a SQUID susceptometer in the 2−300 K range, giving room-temperature values of $\chi_M T$ of 0.70 and 0.67 cm^3 mol^{-1} K, respectively, corresponding to two unpaired electrons per complex, i.e., two nitroxyl groups. These systems show very weak antiferromagnetic coupling at low temperatures, contrary to other systems containing nitroxide radicals which interact directly with a Pd(II) center, and as a result show strong antiferromagnetic coupling.[18,19]

An X-ray crystal structure of **4** was obtained to confirm the presence of the two radical-substituted phosphines. Orange prism crystals were obtained by slow evaporation of a MeCN solution. Crystallographic data appear in Table 1. The molecular structure, shown in Figure 1, is as expected for *trans*-Pd[**2**]$_2$Cl$_2$, with a square planar Pd(II) center and two pendant nitroxide radicals. The NO radical fragment is tilted 13.2° out of the plane of the phenyl to which it is joined. Note that the radical-substituted phosphine **2** cannot be isolated in the solid state in the absence of a coordinating metal.[16] Phosphine **2** has also been stabilized by coordination to a gold(I) center.[20] The Pd−Cl and Pd−P bond lengths of 2.2865(7) and 2.3298(6) Å, respectively (Table 2), are comparable to those found in the parent compound $PdCl_2(PPh_3)_2$, illustrating that the addition of a remote radical group does not significantly alter the coordination sphere of the metal. This important point is one requirement for the application of the spin-labeling technique: that the spin label should be noninvasive. The N−O bond length of 1.286(3) Å is typical of those found in other *t*-BuNO systems.[21]

The room-temperature EPR of the phosphine ligands **1** and **2** in solution are shown in Figure 2, with the EPR spectra of **3** and **4** below them. The EPR of the free ligands show five- and three-line patterns for **1** and **2**, respectively, as expected for coupling to two (**1**) and one (**2**) nitrogen atoms (Figure 2). Note that fine structure is easily observable in the case of **2**, attributable to delocalization of the unpaired electron through the phenyl ring and its consequent coupling to the two sets of protons and the phosphorus atom;[16] this is much weaker in nitronyl nitroxide derivatives. When comparing the free radical ligands with their palladium complexes, it is immediately obvious that coupling is observed between the two remote pendant radicals on

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Table 1. Summary of Crystallographic Data

	4[a]	**5**[b]
formula	$C_{44}H_{46}Cl_2N_2O_2P_2Pd$	$C_{25}H_{28}ClNOPPd$
fw	874.11	531.30
color, habit	orange, block	orange, plate
crystal system	triclinic	orthorhombic
space group	$P\bar{1}$	*Pbca*
a, Å	10.1431(13)	18.8681(5)
b, Å	10.7121(10)	12.9784(7)
c, Å	11.540(2)	19.3052(7)
α, deg	65.461(2)	90
β, deg	73.033(2)	90
γ, deg	64.194(4)	90
V, Å^3	1017.4(2)	4727.4(3)
Z	1	8
ρ_{calc}, g/cm^3	1.427	1.493
F(000)	450	2168
T (K)	180	173
radiation	Mo	Mo
μ, cm^{-1}	7.05	9.82
crystal size, mm	0.15 × 0.20 × 0.25	0.08 × 0.06 × 0.02
transmission factors	0.8401−1.00	0.8832−1.00
$2\theta_{max}$, deg	61.1	50
total no. of reflns	9378	24651
no. of unique reflns	4692	4178
R_{merge}	0.043	0.050
no. with $I \geq x\sigma(I)$[c]	3232	3383
no. of variables	241	402
R, $wR2$ ($I \geq x\sigma(I)$)[c]	0.034, 0.029	0.038, 0.071
R, $wR2$ (all data)	0.061, 0.062	0.056, 0.077

[a] Rigaku/ADSC CCD diffractometer, detector swing angle −10.0°, aperture 94.0 × 94.0 mm at a distance of 38.86 mm from the crystal, Mo Kα radiation ($\lambda = 0.71073$ Å), graphite monochromator, function minimized $\sum w(|F_o{}^2 - F_c{}^2|)^2$, where $w^{-1} = \sigma^2(F_o{}^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = (\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2)^{1/2}$. [b] Siemens SMART CCD diffractometer, Mo Kα ($\lambda = 0.71073$ Å), function minimized $\sum w(|F_o{}^2 - F_c{}^2|)^2$ where $w^{-1} = \sigma^2(F_o{}^2)$, $R = \sum|F_o - |F_c|/\sum|F_o|$, $wR2 = \sum|(w^{1/2}(F_o - F_c)|/\sum|(w)^{1/2}F_o|$. [c] $x = 3$ (Rigaku); $x = 2$ (Siemens)

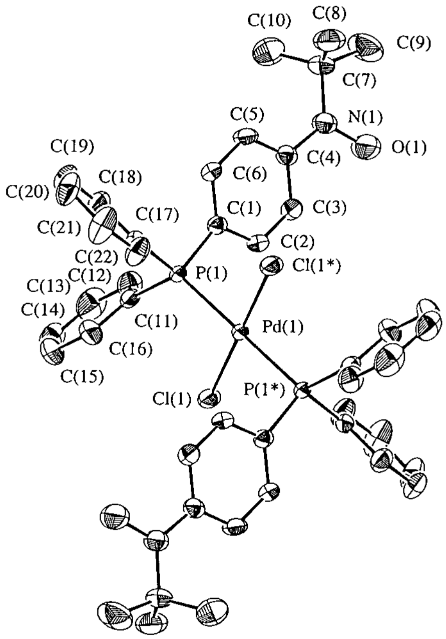

Figure 1. Molecular structure (ORTEP, 33% ellipsoids) and numbering scheme for Pd[**2**]$_2$Cl$_2$ (**4**).

Table 2. Selected Bond Lengths and Angles for *trans*-Bis[(*p*-*t*-BuNO-phenyl)diphenylphosphine]-dichloropalladium(II), Pd[2]$_2$Cl$_2$ (4)

Pd(1)−Cl(1)	2.2865(7)	Pd(1)−P(1)	2.3298(6)
P(1)−C(1)	1.808(2)	P(1)−C(11)	1.821(3)
P(1)−C(17)	1.819(3)	N(1)−O(1)	1.286(3)
N(1)−C(4)	1.420(3)	N(1)−C(7)	1.488(3)
Cl(1)−Pd(1)−Cl(1)[a]	180.0	Cl(1)−Pd(1)−P(1)	92.15(2)
Cl(1)−Pd(1)−P(1)[a]	87.85(2)	P(1)−Pd(1)−P(1)[a]	180.0
Pd(1)−P(1)−C(1)	105.08(8)	Pd(1)−P(1)−C(11)	117.89(8)
Pd(1)−P(1)−C(17)	117.30(9)	C(1)−P(1)−C(11)	105.56(12)
C(1)−P(1)−C(17)	108.45(11)	C(11)−P(1)−C(17)	101.84(12)
O(1)−N(1)−C(4)	115.5(2)	O(1)−N(1)−C(7)	118.4(2)
C(4)−N(1)−C(7)	126.0(2)	N(1)−C(4)−C(3)	117.3(2)

[a] Symmetry operation: 1−*x*, 1−*y*, −*z*.

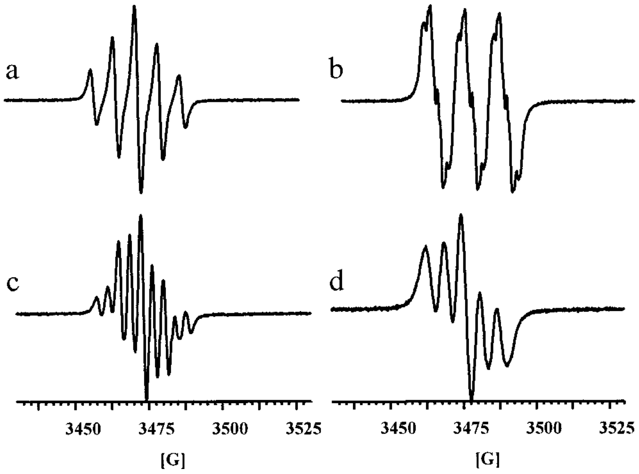

Figure 2. EPR spectra for phosphine ligands **1** (a) and **2** (b) and the corresponding PdCl$_2$(phosphine)$_2$ adducts **3** (c) and **4** (d) recorded in CH$_2$Cl$_2$ solutions at 298 K (microwave power 0.2 mW, modulation amplitude 0.5 G, $\nu = 9.75$ GHz).

the phosphines.[21,22] The spectra of **3** and **4** show respectively a nine- and five-line pattern with apparent hyperfine coupling constants of 3.7 and 6.2 G. The position of these absorption features as well as the multiplicity of the spectra is characteristic of an exchange coupling larger than the hyperfine coupling ($J > a_N$). However, the relative amplitude ratios are different from that expected for strong exchange coupling ($J \gg a_N$), i.e., 1:4:10:16:19:16:10:4:1 and 1:2:3:2:1 ratios for four and two equivalent nitrogen atoms, respectively.[23] This coupling, as it is observed in dilute solution at room temperature, is intramolecular in origin. Coordination to the metal center of two spin-labeled phosphines thus generates the coupling pattern shown. Hence, using the spin-labeled phosphines, it is possible to determine how many phosphines are coordinated to a metal center (an important factor in catalytic systems) from observing the coupling pattern in the EPR spectrum. Furthermore, the high sensitivity of EPR allows this determination to be accomplished at much lower concentrations of metal complex (10^{-6} M) than would be possible with the more commonly used NMR techniques.[24] The observation of changes in coupling patterns between spin labels has been used with polyazamacrocycles,[25] calixarenes,[26,27] and acyclic

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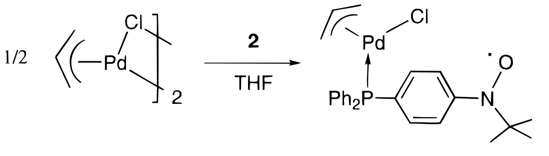
glycols[28,29] as a sensor for the binding of metal cations and other substrates.

A simple example of this principle in action is given in eq 2. It is well-known that Pd−phosphine complexes undergo ligand exchange in the presence of excess phosphine. This reaction is often investigated by ^{31}P NMR spectroscopy; the spin-labeled phosphines presented here offer another method to study, in particular, the case of ligand self-exchange.

$$\mathrm{Pd}[\mathbf{2}]_2\mathrm{Cl}_2 \overset{\mathbf{L}}{\rightleftharpoons} \mathrm{Pd}[\mathbf{2}](\mathbf{L})\mathrm{Cl}_2 + \mathbf{2} \overset{\mathbf{L}}{\rightleftharpoons} \mathrm{Pd}(\mathbf{L})_2\mathrm{Cl}_2 + \mathbf{2} \qquad (2)$$

Thus, addition of an excess of PPh$_3$ to a solution of **4** has two immediate consequences. First, within a few seconds the color of the solution changes from orange to red-pink, the color of free phosphine **2**. More importantly, the EPR spectrum of the reaction mixture collapses from five lines to three. This loss of coupling indicates that at least one spin-labeled phosphine has been displaced from the metal center. This technique could potentially be applied to more complex systems.

(η^3-Allyl)palladium(II) and (η^6-*p*-Cymene)ruthenium(II) Complexes with [(*p*-*t*-BuNO−Ph)PPh$_2$]. In order for spin-labeled phosphines to be of use in organometallic systems, it is important to illustrate their stability in the presence of organometallic fragments. Two well-known families of organometallic catalysts are (η^3-allyl)Pd[30] and (η^6-arene)Ru[31] compounds. Their use in organic synthesis is well-documented, but the reaction mechanisms they are involved in are still under investigation.[32−34] Thus the reactions of **2** with [(η^3-C$_3$H$_5$)PdCl]$_2$ and [(η^6-*p*-cymene)RuCl$_2$]$_2$ were examined. Addition of the phosphine **2** to solutions of these dimers gave bright red-orange solutions, from which the mononuclear products (η^3-C$_3$H$_5$)Pd[**2**]Cl (**5**) and (η^6-*p*-cymene)Ru[**2**]Cl$_2$ (**6**) were isolated in high yield (eqs 3 and 4). Significantly, both complexes are stable with respect to destruction of the pendant radical (e.g., by redox processes).



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(3)

Magnetic susceptibility measurements confirm the stability of the complexes, with values of $\chi_M T$ of 0.35 and 0.37 cm^3 mol^{-1} K for **5** and **6**, respectively, corresponding to one unpaired electron per complex. The EPR spectra of both systems show the standard three-line pattern with fine structure typical of phenyl−aminoxyl moieties and are essentially unchanged relative to the EPR spectrum of the free ligand. Contrary to complexes **3** and **4**, there is only one phosphine bound to the metal center, and hence, no inter-radical coupling is observed.

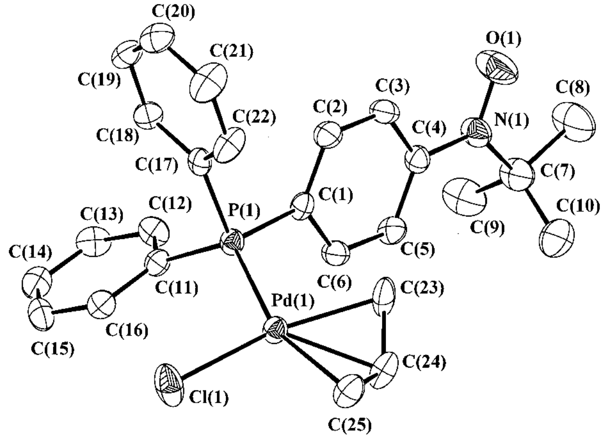
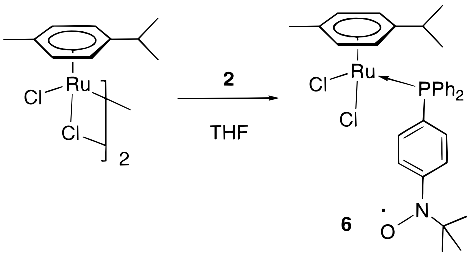


Figure 3. Molecular structure (ORTEP, 33% ellipsoids) and numbering scheme for (η^3-C$_3$H$_5$)Pd[**2**](Cl) (**5**). The minor occupancy fragment of the η^3-allyl group has been removed for clarity.



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(4)

The ^{1}H NMR spectra of complexes **5** and **6** are more informative than those of complexes **3** and **4** presented above by virtue of the presence of organometallic fragments. The resonances in the spectra are broadened as expected, but still provide compound fingerprints. For compound **5**, in addition to the phenyl resonances (from the nonsubstituted phenyl rings) at δ = 8.5, 7.5, and 7.2 ppm and the broad feature at δ = −2 ppm (*t*-Bu), a broad resonance attributable to the terminal allyl protons is visible at δ = 6.2 ppm. The single central proton of the η^3-allyl group could not be unambiguously assigned. For complex **6**, the phosphine phenyl resonances occur at δ = 8.4, 7.35, and 7.0 ppm. The phenyl protons of the η^6-*p*-cymene fragment are at δ = 5.0 ppm, while the resonances assignable to the methyl and isopropyl (C*H*$_3$ and *H*) protons of the *p*-cymene are at δ = 1.88, 1.13, and 3.0 ppm, respectively. Note that the resonances of the organometallic fragments are broadened, indicating the effect of the remote aminoxyl radical on each proton, but only slightly shifted with respect to the corresponding PPh$_3$ derivative.[35,36]

The X-ray crystal structure of complex **5** was solved; the result is shown in Figure 3. It confirms the presence of both the spin-labeled phosphine and an η^3-allyl fragment in the same molecule. The aminoxyl moiety is a mere 4.4° out of the plane of the phenyl to which it

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Table 3. Selected Bond Lengths and Angles for [(*p*-*t*-BuNO-phenyl)diphenylphosphine]-(η^3-C_3H_5)chloropalladium(II), (η^3-C_3H_5)Pd[2](Cl) (5)

Pd(1)−Cl(1)	2.3717(10)	Pd(1)−P(1)	2.3095(9)
Pd(1)−C_{allyl}(av)	2.16	P(1)−C(1)	1.833(3)
P(1)−C(11)	1.839(3)	P(1)−C(17)	1.830(4)
N(1)−O(1)	1.278(4)	N(1)−C(4)	1.424(4)
N(1)−C(7)	1.517(5)	C(23)−C(24)	1.42(2)
C(24)−C(25)	1.39(2)		
P(1)−Pd(1)−Cl(1)	103.82(3)	Pd(1)−P(1)−C(1)	112.91(11)
Pd(1)−P(1)−C(11)	119.93(11)	Pd(1)−P(1)−C(17)	112.22(11)
C(1)−P(1)−C(11)	103.2(2)	C(1)−P(1)−C(17)	103.9(2)
C(11)−P(1)−C(17)	103.0(2)	O(1)−N(1)−C(4)	116.3(3)
O(1)−N(1)−C(7)	117.7(3)	C(4)−N(1)−C(7)	126.0(3)
N(1)−C(4)−C(3)	118.0(3)	C(23)−C(24)−C(25)	120.1(14)

is bound. The Pd−Cl and Pd−P bond lengths of 2.3717(10) and 2.3095(9) Å, respectively (Table 3), compare well with those found in other Pd−allyl complexes.[37,38] The N−O bond length of 1.278(4) Å is very similar to that found in complex **2** above. Again, it is clear that the incorporation of an organic radical group remote to the metal center does not perturb the coordination sphere of the metal. Additionally, the structure illustrates the stability of the organometallic fragment in the presence of a pendant organic radical.

Conclusions

Triphenylphosphine ligands substituted with nitronyl nitroxide or *N*-aminoxyl moieties, persistent organic radicals, can be considered as spin-labeled phosphines. Their incorporation into $PdCl_2$(phosphine)$_2$ complexes and the subsequent coupled EPR spectra showed their possible utility in determining the number of phosphines bound to a metal center in low-concentration solutions. The spin-labeled phosphines also formed stable complexes with organometallic Pd(II) and Ru(II) systems. Significantly, all compounds were stable in solution over periods of several hours to days with respect to the destruction of the radical moiety. The use of these radical-substituted phosphines is perhaps the easiest and most generally applicable method for introducing a spin label into organometallic complexes.

Experimental Section

General Procedures. Unless otherwise stated all manipulations were performed in a nitrogen atmosphere using standard Schlenk techniques. Hexanes and CH_2Cl_2 were refluxed over CaH_2 under a nitrogen atmosphere and distilled prior to use; diethyl ether and THF were distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Phosphines **1H**, **1**,[13,14] and **2H**[15,16] and [(η^6-*p*-cymene)$RuCl_2$]$_2$[35] were prepared according to published procedures. $PdCl_2(MeCN)_2$ was prepared by dissolving $PdCl_2$ in MeCN. The resulting solution was used directly for subsequent synthetic steps. Phosphine **2H** was selectively oxidized at the N−OH group by Ag_2O in CH_2Cl_2 at room temperature within 15 min to give radical phosphine **2**, which was used in situ. All other reagents were obtained from commercial sources and used as received. Magnetic susceptibility data were collected using a SQUID MPMS-5S magnetometer in the range 2−300 K at 1000 Oe field strength. The data were corrected for the diamagnetism of the constituent atoms.

Synthesis of Bis[(*p*-nitronyl nitroxide-phenyl)diphenylphosphine]dichloropalladium(II), Pd[1]$_2$Cl$_2$ (3). Method A. Phosphine **1** (0.045 g, 0.107 mmol) was dissolved in CH_2Cl_2 (10 mL) in a round-bottomed flask. The resulting blue solution was added dropwise to a yellow MeCN solution (10 mL) of $PdCl_2$ (0.010 g, 0.056 mmol) to give a green solution, which was stirred for 3 h. The solvent was then removed in vacuo to give a green solid, which was redissolved in CH_2Cl_2/hexanes. Slow evaporation of this solution gave microcrystalline **3** (0.030 g, 53%).

Method B. $PdCl_2$ (0.021 g, 0.118 mmol) was suspended in MeCN (15 mL) and stirred overnight to give $PdCl_2(MeCN)_2$ as a yellow solution. A solution of phosphine **1H** (0.100 g, 0.238 mmol) in MeCN (10 mL) was added, with stirring, to yield a pale yellow precipitate. After stirring for 30 min, the solvents were removed in vacuo to give crude **3H** as a pale yellow solid. The crude solid was resuspended in CH_2Cl_2 (15 mL), and a solution of $NaIO_4$ (0.075 g, 0.352 mmol) in H_2O (10 mL) was added slowly. After 1 h of vigorous stirring, a green color had developed in the organic layer. The mixture was stirred overnight, during which the insoluble **3H** completely reacted to give a dark green solution in the organic layer, which was separated and dried with $MgSO_4$, and the solvent was removed in vacuo. The residue was redissolved in CH_2Cl_2/hexanes, and subsequent slow evaporation gave green microcrystalline **3** (0.095 g, 79%). Despite drying under vacuum, the crystals retained CH_2Cl_2, as indicated by ^1H NMR. Anal. Calcd for $C_{50}H_{52}Cl_2N_4O_4P_2Pd\cdot 0.75CH_2Cl_2$: C, 56.65; H, 5.01; N, 5.21. Found: C, 56.66; H, 5.04; N, 5.05. ^1H NMR ($CDCl_3$, ppm): $\delta = 7.6, 7.25$ (Ph). IR (KBr): 3054, 2987, 1482, 1435, 1387, 1365 (νNO), 1304, 1165, 1133, 1096, 832, 743, 703 cm^{-1}. EPR (CH_2Cl_2, 298 K): 9-line pattern ($g = 2.006$; $a_N = 3.7$ G).

Synthesis of Bis[(*p*-*t*-BuNO-phenyl)diphenylphosphine]dichloropalladium(II), Pd[2]$_2$Cl$_2$ (4). $PdCl_2$ (0.019 g, 0.107 mmol) was suspended in MeCN (15 mL) and stirred overnight to give $PdCl_2(MeCN)_2$ as a yellow solution. Separately, phosphine **2H** (0.075 g, 0.214 mmol) was dissolved in CH_2Cl_2 (10 mL) and solid Ag_2O (0.05 g, 0.214 mmol) was added, with stirring, yielding a bright orange solution. After stirring for 15 min, the resulting solution of phosphine radical **2** was filtered through Celite directly into the Pd-containing solution to give an orange-yellow solution, which was stirred for an additional hour, then filtered through Celite. The solvents were then removed in vacuo to give an orange solid. The crude product was triturated with CCl_4 to remove an impurity of $PdCl_2$[**2**][**2H**] (i.e., a monoradical species) and the remaining solid dried to give Pd[**2**]$_2$Cl$_2$ (**4**) (0.071 g, 76%). Recrystallization by slow evaporation of a concentrated MeCN solution gave orange prism crystals suitable for X-ray crystallographic analysis. Anal. Calcd for $C_{44}H_{46}Cl_2N_2O_2P_2Pd$: C, 60.46; H, 5.30; N, 3.20. Found: C, 60.02; H, 5.26; N, 3.12. ^1H NMR ($CDCl_3$, ppm): $\delta = 8.6$ (4H, o-Ph), 7.6 (4H, m-Ph), 7.4 (2H, p-Ph), −1.5 (9H, *t*-Bu). IR (KBr): 3048, 2981, 2928, 1481, 1437, 1186 (νNO), 1098, 819, 733, 692 cm^{-1}. EPR (CH_2Cl_2, 298 K): 5-line pattern ($g = 2.005$; $a_N = 6.2$ G).

Synthesis of [(*p*-*t*-BuNO-phenyl)diphenylphosphine](η^3-C_3H_5)chloropalladium(II), (η^3-C_3H_5)Pd[2](Cl) (5). Phosphine **2H** (0.070 g, 0.200 mmol) was dissolved in CH_2Cl_2 (10 mL) in a foil-protected round-bottomed flask. To this was added solid Ag_2O (0.046 g, 0.200 mmol). Upon stirring for 5 min an orange color developed, and after 15 min the mixture was filtered through Celite. The solution of **2** was added dropwise to a 10 mL THF solution of [(η^3-C_3H_5)PdCl]$_2$ (0.037 g, 0.100 mmol) to give a brilliant red solution. The mixture was stirred for 2 h and then filtered through Celite, after which the solvent was removed in vacuo to give a red oil. Recrystallization from minimum CH_2Cl_2/Et_2O gave deep red crystals of **5** (0.095 g, 89%) suitable for X-ray analysis. Anal. Calcd for $C_{25}H_{28}ClNOPPd$: C, 56.51; H, 5.31; N, 2.64. Found: C, 56.41;

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H, 5.36; N, 2.67. ^{1}H NMR ($CDCl_3$, ppm): $\delta = 8.5$ (4H, o-Ph), 7.7 (4H, m-Ph), 7.25 (2H, p-Ph), 6.2 (4H, $CH_2{-}CH{-}CH_2$), -1.5 (broad, *t*-Bu). IR (KBr): 3044, 2986, 1478, 1435, 1407, 1302, 1237, 1179, 1096, 1207, 827, 816 cm^{-1}. EPR (CH_2Cl_2, 298 K): 3-line pattern ($g = 2.005$; $a_N = 12.1$ G).

Synthesis of [(*p*-*t*-BuNO-phenyl)diphenylphosphine](η^6-*p*-cymene)dichlororuthenium(II), (η^6-*p*-cymene)Ru[2]Cl_2 (6). Phosphine **2H** (0.033 g, 0.095 mmol) was dissolved in CH_2Cl_2 (10 mL) in a foil-protected round-bottomed flask. To this was added solid Ag_2O (0.022 g, 0.095 mmol). Upon stirring for 5 min an orange color developed, and after 15 min the mixture was filtered through Celite. This solution of **2** was added dropwise to a 15 mL CH_2Cl_2 solution of [(η^6-*p*-cymene)-$RuCl_2]_2$ (0.030 g, 0.048 mmol) to give a red-orange solution, which was stirred for 2 h. Subsequently, the solvent was removed in vacuo to give a red powder. Slow evaporation of a CH_2Cl_2/Et_2O solution of this crude product gave **6** (0.057 g, 87%) as very thin plate crystals. Anal. Calcd for $C_{32}H_{37}Cl_2NOPRu$: C, 58.72; H, 5.70; N, 2.14. Found: C, 58.45; H, 5.86; N, 2.07. ^{1}H NMR ($CDCl_3$, ppm): $\delta = 8.4$ (4H, o-Ph), 7.35 (4H, m-Ph), 7.0 (2H, p-Ph), 5.0 (4H, cymene), 3.0 (1H, Me_2CH), 1.88 (3H, *Me*Ph), 1.13 (6H, CH-*Me*$_2$). IR (KBr): 3061, 2959, 1481, 1435, 1262, 1185, 1096, 1058, 1032, 823, 800 cm^{-1}. EPR (CH_2Cl_2, 298 K): 3-line pattern ($g = 2.005$; $a_N = 12.0$ G).

X-ray Crystallographic Analysis. Bis[(*p*-*t*-BuNO-phenyl)diphenylphosphine]dichloropalladium(II), Pd[2]$_2$Cl$_2$ (4). Data Collection and Processing:[39] Crystallographic data appear in Table 1. A crystal of **4** was mounted on a glass fiber and measured on a Rigaku/ADSC CCD diffractometer at 180(1) K. Data were collected in 0.50° oscillations with 20.0 s exposures. A sweep of data was done using ϕ oscillations from 0.0° to 190.0° at $\chi = -90°$, and a second sweep was performed using ω oscillations between $-23.0°$ and 18.0° at $\chi = -90°$. The final unit-cell parameters were obtained by conducting least-squares calculations on 6445 strong reflections (2θ range 4.0$-$61.1). The data were processed and corrected for Lorentz and polarization effects and absorption.

Structure Analysis and Refinement. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The metal atom lies on a center of symmetry; thus the coordination group is exactly planar. Full-matrix least-squares refinement was conducted with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions (C$-$H = 0.98 Å, $B_{iso} = 1.2B$(parent atom)). Neutral atom scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography*.[40] Selected bond lengths and angles are found Table 2.

[(*p*-*t*-BuNO-phenyl)diphenylphosphine](η^3-C_3H_5)chloropalladium(II), (η^3-C_3H_5)Pd[2](Cl) (5). Data Collection and Processing. Crystallographic data are in Table 1. A crystal of **5** was mounted on a glass fiber and measured on a Siemens SMART CCD system at 173(2) K. A randomly oriented region of reciprocal space was surveyed to the extent of 1.3 hemispheres and to a resolution of 0.84 Å. Three major swaths of frames were collected with 0.30 steps in ω. The data were processed using SAINT.[41] Final cell constants were calculated from the *xyz* centroids of 8192 reflections from the actual data after integration. The data were corrected for absorption using SADABS (Sheldrick, 1996).

Structure Analysis and Refinement. A direct-methods solution located most non-hydrogen atoms. The remaining atoms were found by conducting full-matrix least-squares and difference Fourier cycles. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms, except for the hydrogens of the disordered allyl group, were located from the difference map and were refined with isotropic displacement paramaters. For the allyl fragment occupying the major site (77% occupancy), hydrogen atoms were refined at a fixed distance. For the minor site the hydrogen atoms were placed in ideal positions and refined as riding atoms with individual or group (H25c and H25d) isotropic displacement parameters. Selected bond lengths and angles are found in Table 3.

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Supporting Information Available: Complete tables of bond lengths and bond angles, atomic coordinates, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes. This material is available free of charge via the Internet at http://pubs.acs.org.

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