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Coordination chemistry of $[\text{CH}(\text{P}(\text{S})\text{Ph}_2)_2]^-$: X-ray diffraction studies of *S,S*-chelate complexes of iridium and rhodium

Jane Browning, Gordon W. Bushnell, Keith R. Dixon and Robert W. Hiltz

Department of Chemistry, University of Victoria, Victoria, B.C. V8W 3P6 (Canada)

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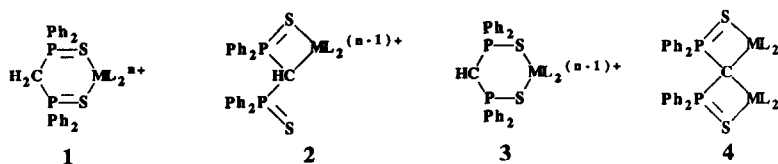
Abstract

Reactions of the chloro-bridged complexes, $[\text{M}_2\text{Cl}_2(\text{cod})_2]$, $\text{M} = \text{Ir}$ or Rh , with $\text{CHR}(\text{P}(\text{S})\text{Ph}_2)_2$, $\text{R} = \text{H}$ or Me , provide a synthetic route to the cations, $[\text{M}(\text{cod})(\text{CHR}(\text{P}(\text{S})\text{Ph}_2)_2\text{-S,S})]^+$, which are isolated as fluoroborate or perchlorate salts. Treatment of these products with sodium hydride results in facile deprotonation to the neutral complexes, $[\text{M}(\text{cod})(\text{CR}(\text{P}(\text{S})\text{Ph}_2)_2\text{-S,S})]$, and when $\text{R} = \text{H}$, the neutral complexes are also accessible via reactions of $[\text{M}_2\text{Cl}_2(\text{cod})_2]$ with $\text{Li}[\text{CH}(\text{P}(\text{S})\text{Ph}_2)_2]$. The complexes, $[\text{Ir}(\text{cod})(\text{CH}(\text{P}(\text{S})\text{Ph}_2)_2\text{-S,S})]$ and $[\text{Rh}(\text{cod})(\text{CH}(\text{P}(\text{S})\text{Ph}_2)_2\text{-S,S})]$, crystallize in the *P*1 (No. 2) space group ($Z = 2$) with respective unit cells: $a = 11.570(4)$, $b = 15.122(2)$, $c = 9.919(3)$ Å, $\alpha = 79.86(4)$, $\beta = 64.87(3)$, $\gamma = 97.94(4)^\circ$; and $a = 11.571(16)$, $b = 15.078(2)$, $c = 9.869(2)$ Å, $\alpha = 100.16(1)$, $\beta = 64.97(1)$, $\gamma = 82.10(1)^\circ$. Both structures consist of puckered 6-membered rings formed by coordination of the disulfide ligands via two sulfur atoms to the metal center. The rings lie in distorted boat conformations with the prows occupied by one sulfur and one phosphorus and the metal atoms in one side.

Introduction

Coordination complexes of $\text{CH}_2\{\text{P}(\text{S})\text{Ph}_2\}_2$, and related bis(phosphine)sulfide ligands, have been known for approximately 20 years, but they nevertheless remain an area of active research interest [1–21]. A variety of coordination modes is possible and complexes involving monodentate *S* [6,17], bidentate *S,S* [7], and bridging *S,S* [8], have all been reported. The ligands are loosely analogous to acetylacetone (acac) [22] and its dithio analog (SacSac) [23], but differ in forming stable complexes of the neutral ligands, whereas the coordination chemistry of acac and SacSac is essentially entirely that of the derived anions. It follows that the acidity (reactivity) of the methylene protons of coordinated $\text{CH}_2\{\text{P}(\text{S})\text{Ph}_2\}_2$ and the consequent complexes of $[\text{CH}(\text{P}(\text{S})\text{Ph}_2)_2]^-$ are of considerable interest.

Correspondence to: Dr. K.R. Dixon, Department of Chemistry, University of Victoria, Victoria, B.C., Canada V8W 3P6.



Scheme 1. Structures of $\text{CH}_2(\text{P}(\text{S})\text{Ph}_2)_2$ and $[\text{CH}(\text{P}(\text{S})\text{Ph}_2)_2]^-$ complexes.

Our previous work [11,24] has shown that in platinum chemistry, the most usual result of deprotonation of $\text{CH}_2(\text{P}(\text{S})\text{Ph}_2)_2$ complexes is a reorganization from *S,S*-chelates (Scheme 1, structure 1) to *C,S* bonded complexes (2) rather than a simple deprotonation to complexes of type 3. We have also prepared the novel dimer, 4, which arises by double deprotonation of a bis(phosphine disulfide) ligand [19]. Simple *S,S* complexes (3) can be prepared for platinum [24] and some other metals [2], but they have been much less extensively studied. In particular, no *S,S*-bonded complex of $[\text{CH}(\text{P}(\text{S})\text{Ph}_2)_2]^-$ has been studied by X-ray diffraction.

The present paper reports results of deprotonation of the iridium and rhodium cations, $[\text{M}(\text{cod})\{\text{CH}_2(\text{P}(\text{S})\text{Ph}_2)_2\text{-S,S}\}]^+$, $\text{cod} = 1,4\text{-cyclooctadiene}$, including X-ray diffraction studies of the resulting complexes, $[\text{M}(\text{cod})\{\text{CH}(\text{P}(\text{S})\text{Ph}_2)_2\text{-S,S}\}]$. The retention of the *S,S* coordination mode contrasts with the conversion to *C,S* coordination in platinum complexes, and the structural results present a useful comparison with the very recent structural report on the parent cations, $[\text{M}(\text{cod})\{\text{CH}_2(\text{P}(\text{S})\text{Ph}_2)_2\text{-S,S}\}]^+$ [20].

Experimental

Synthesis and spectroscopy

Data relating to the characterization of the complexes are given in the tables in the Results section and in the preparative descriptions below. Microanalysis was by the Canadian Microanalytical Service, Vancouver, B.C., Canada. ^{31}P and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in appropriate solvents at 101.3 and 62.9 MHz, respectively, using a Bruker WP250 Fourier transform spectrometer locked to the solvent deuterium resonance. For both nuclei, protons were decoupled by broad band ("noise") irradiation at appropriate frequencies. ^{31}P chemical shifts were measured relative to external $\text{P}(\text{OMe})_3$ and are reported in parts per million relative to 85% H_3PO_4 using a conversion factor of +141 ppm. ^{13}C chemical shifts are reported in ppm relative to $\text{Si}(\text{CH}_3)_4$. Positive values are deshielded relative to the references.

All operations were carried out at ambient temperature (approx. 25°C) under an atmosphere of dry nitrogen using standard Schlenk tube techniques. Solvents were dried by reflux over appropriate reagents (molecular sieves or K_2CO_3 for acetone, and potassium/benzophenone for diethyl ether, tetrahydrofuran, toluene, benzene and hexane) and were distilled under nitrogen prior to use. Recrystallizations from solvent pairs were by dissolution of the complex in the first solvent (using about double the volume required for complete solution) followed by dropwise addition or layering of sufficient second solvent to cause turbidity at ambient temperature. Crystallization was then completed either by continued very slow dropwise addi-

tion of the second solvent or by setting the mixture aside at a reduced temperature.

The metal complexes, $[M_2Cl_2(cod)_2]$, $M = Rh$ or Ir , were prepared as previously described [25,26]. The ligand $CH_2\{P(S)Ph_2\}_2$, has been prepared previously by reaction of $[CH_2\{P(S)Ph_2\}]^-$ with Ph_2PCl followed by heating with sulfur [10], but we usually preferred to obtain it by the simpler expedient of heating $CH_2\{PPh_2\}_2$ with 2 molar equiv. of elemental sulphur under reflux in benzene for 2 h. $CHMe\{P(S)Ph_2\}_2$ [27] was obtained by treating a tetrahydrofuran solution of $Li[CH\{P(S)Ph_2\}_2]$ with 1 molar equiv. of iodomethane.

$[Rh(cod)\{CHMe\{P(S)Ph_2\}_2-S,S\}]BF_4$. A solution of $CHMe\{P(S)Ph_2\}_2$ (0.19 g, 0.40 mmol) in acetone (10 mL) was added dropwise to a stirred solution of $[Rh_2Cl_2(cod)_2]$ (0.10 g, 0.20 mmol) and $NaBF_4$ (0.056 g, 0.50 mmol) in acetone (20 mL). After 2 h, the solution was filtered to remove precipitated $NaCl$. Solvent was removed from the filtrate *in vacuo* and the residue recrystallized from tetrahydrofuran/diethyl ether to give $[Rh(cod)\{CHMe\{P(S)Ph_2\}_2-S,S\}]BF_4$ as yellow crystals (0.26 g, 0.34 mmol). Anal. Found: C, 53.3; H, 4.85. $C_{34}H_{36}BF_4P_2RhS_2$ calc.: C, 53.7; H, 4.77%.

$[M(cod)\{CH_2\{P(S)Ph_2\}_2-S,S\}]Z$ ($M = Rh$, $Z = ClO_4$; $M = Ir$, $Z = BF_4$). These complexes have been prepared previously, using reactions of $CH_2\{P(S)Ph_2\}_2$ with $[M_2Cl_2(cod)_2]/AgClO_4$ [5] or $[M(cod)_2]ClO_4$ [20]. We preferred to prepare them using $[M_2Cl_2(cod)_2]$ with $NaClO_4 \cdot H_2O$ or $NaBF_4$ in procedures similar to the example above.

$[Ir(cod)\{CH\{P(S)Ph_2\}_2-S,S\}]$. *Method A*: Sodium hydride (0.08 g, 2.7 mmol, 80% in oil) was added to a stirred solution of $[Ir(cod)\{CH_2\{P(S)Ph_2\}_2-S,S\}]BF_4$ (0.25 g, 0.30 mmol) in tetrahydrofuran (10 mL). After 2 h, the reaction mixture was filtered to remove unreacted NaH . Solvent was removed from the filtrate *in vacuo* and the residue recrystallized from tetrahydrofuran/hexane to give $[Ir(cod)\{CH\{P(S)Ph_2\}_2-S,S\}]$ as yellow crystals (0.16 g, 0.21 mmol). Anal. Found: C, 53.8; H, 4.68. $C_{33}H_{33}P_2IrS_2$ calc.: C, 53.0; H, 4.45%.

Method B: A slight excess (approx. 1.1–1.2 molar equiv.) of *n*-butyl lithium (1.5 *M* in hexane) was added dropwise to a stirred solution of $CH_2\{P(S)Ph_2\}_2$ (0.13 g, 0.29 mmol) in tetrahydrofuran (5 mL). ^{31}P and ^{13}C NMR spectra confirmed that $Li[CH\{P(S)Ph_2\}_2]$ was the sole phosphorus containing product. The solution was added dropwise to a stirred solution of $[Ir_2Cl_2(cod)_2]$ (0.10 g, 0.15 mmol) in tetrahydrofuran (10 mL). After 3 h, the volume was reduced to about 2 mL by removal of solvent *in vacuo*, and $[Ir(cod)\{CH\{P(S)Ph_2\}_2-S,S\}]$ was identified as the only product by ^{31}P NMR spectroscopy.

$[Rh(cod)\{CH\{P(S)Ph_2\}_2-S,S\}]$. This complex was prepared by procedures similar to A and B above. Recrystallization was from tetrahydrofuran/hexane. Anal. Found: C, 59.5; H, 5.17. $C_{33}H_{33}P_2RhS_2$ calc.: C, 60.2; H, 5.05%.

$[Rh(cod)\{CMe\{P(S)Ph_2\}_2-S,S\}]$. This complex was prepared by a procedure similar to A above. Method B was not successful for this complex because *n*-butyl lithium apparently failed to deprotonate $CHMe\{P(S)Ph_2\}_2$. Recrystallization was from tetrahydrofuran/diethyl ether. Anal. Found: C, 60.6; H, 5.46. $C_{34}H_{35}P_2RhS_2$ calc.: C, 60.7; H, 5.25%.

Protonation reactions. These were carried out on a small scale in 10 mm NMR tubes using approximately 1 molar equiv. of $HBF_4 \cdot Et_2O$ in either diethyl ether or tetrahydrofuran solution. Monitoring of the reactions by ^{31}P NMR spectroscopy

indicated that all of the complexes, $[\text{M}(\text{cod})\{\text{CR}(\text{P}(\text{S})\text{Ph}_2)_2\text{-S,S}\}]$, were rapidly converted in high yields to the corresponding cations, $[\text{M}(\text{cod})\{\text{CHR}(\text{P}(\text{S})\text{Ph}_2)_2\text{-S,S}\}]^+$.

X-Ray data collection

$[\text{Ir}(\text{cod})\{\text{Ph}_2\text{P}(\text{S})\text{CHP}(\text{S})\text{Ph}_2\}]$ and $[\text{Rh}(\text{cod})\{\text{Ph}_2\text{P}(\text{S})\text{CHP}(\text{S})\text{Ph}_2\}]$ were prepared as described above and crystals suitable for study by X-ray diffraction were grown by recrystallization from hexanes. Preliminary photographic work was carried out with Weissenberg and precession cameras using $\text{Cu-K}\alpha$ radiation. After establishment of symmetry and approximate unit cells, the crystals were transferred to one of two diffractometers (see Table 1) and the unit cells refined by least squares methods employing pairs of centering measurements. During the subsequent data collection, there was no evidence of decomposition of either crystal.

The Picker 4-circle instrument was automated with a PDP11/10 computer and used a θ - 2θ step scan with 160 steps of 0.01° in 2θ , counting for 0.25 s per step. Background measurements were for 20 s at each end of the scan. Each batch of 50 reflections was preceded by the measurement of three standard reflections, and, after application of Lorentz and polarization factors, each batch was scaled to maintain the sum of the standards constant. Absorption corrections were applied by a numerical integration using a Gaussian grid and with the crystal shape defined by perpendicular distances to crystal faces from a central origin.

Measurements on the CAD4 diffractometer used the NRCCAD modification of the Enraf-Nonius program [28], and the "Profile" ω - 2θ scan developed by Grant and Gabe [29]. Three standard reflections were measured every hour to check crystal stability and three others were measured every 400 reflections to check

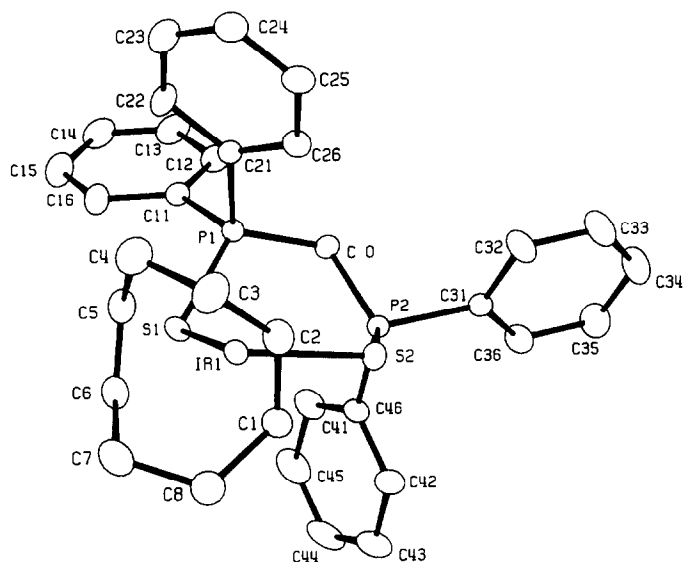


Fig. 1. ORTEP plot of $[\text{Ir}(\text{cod})\{\text{CH}(\text{P}(\text{S})\text{Ph}_2)_2\}]$. The cod ligand is coordinated to iridium via carbons C1, C2, C5, and C6

crystal orientation. Lorentz and polarization factors were applied and the data were corrected for absorption using an empirical method based on the work of North *et al.* [30] as implemented in the CAD4 structure determining package.

Structure solution and refinement

The iridium structure was found and refined using the SHELX-76 program package [31], and the rhodium one using the NRCVAX program [32]. Illustrations were drawn using ORTEP [33]. The atomic scattering factors used were for neutral atoms, with corrections for anomalous dispersion [34]. The structures were solved by direct methods, developed by standard Fourier synthesis procedures using difference maps, and refined by the method of least squares minimizing $\sum w \Delta^2$ where $\Delta = \|F_o| - |F_c\|$. The weights were obtained from counting statistics using $w = 1/(\sigma^2(F) + 0.001F^2)$. All atoms were treated anisotropically. The hydrogen atoms were not located. The final difference maps gave no indication that any material had been overlooked.

Results

The chloro-bridged complexes, $[M_2Cl_2(cod)_2]$ are often convenient starting materials for rhodium and iridium complexes and, in the present instance, they react smoothly with $CHR(P(S)Ph_2)_2$, $R = H$ or Me , under mild conditions to form the cations, $[M(cod)\{CHR(P(S)Ph_2)_2-S,S\}]^+$. In order to facilitate the reaction by precipitation of $NaCl$, and to provide a counter ion, the reactions are carried out in acetone in the presence of $NaClO_4$ or $NaBF_4$. Reactions of the resulting salts with sodium hydride in tetrahydrofuran result in facile deprotonation to form the neutral complexes, $[M(cod)\{CR(P(S)Ph_2)_2-S,S\}]$, and, when $R = H$, these products

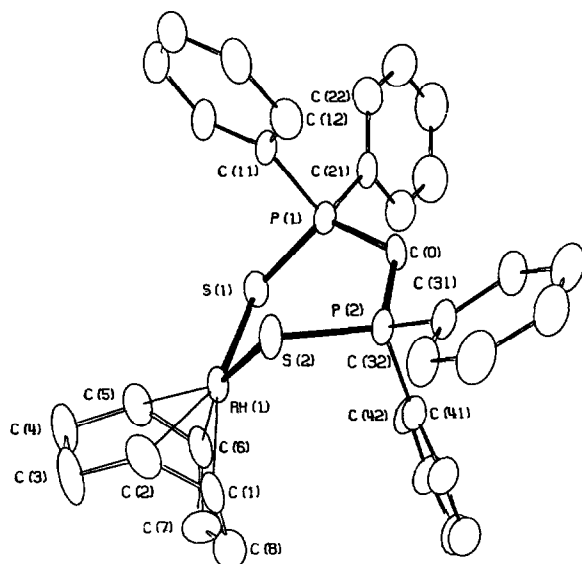


Fig. 2. ORTEP plot of $[Rh(cod)\{CH(P(S)Ph_2)_2\}]$.

Table 1
Crystallographic data

	[Ir(cod){CH(P(S)Ph ₂) ₂ }]	[Rh(cod){CH(P(S)Ph ₂) ₂ }]
Formula	C ₃₃ H ₃₃ P ₂ S ₂ Ir	C ₃₃ H ₃₃ P ₂ S ₂ Rh
FW	747.9	658.6
Space group	<i>P</i> $\bar{1}$ (no 2)	<i>P</i> $\bar{1}$ (no 2)
<i>a</i> (Å)	11.570(4)	11.571(16)
<i>b</i> (Å)	15.122(2)	15.078(2)
<i>c</i> (Å)	9.919(3)	9.869(2)
α (deg)	79.86(4)	100.16(1)
β (deg)	64.87(3)	64.97(1)
γ (deg)	97.94(4)	82.10(1)
<i>V</i> (Å ³)	1502	1492
<i>Z</i>	2	2
Diffractometer	Pickering 4-circle	Enraf-Nonius CAD4
Radiation (λ , Å)	Mo-K α (0.71069)	Mo-K α (0.71069)
μ (cm ⁻¹)	49.76	8.24
Transmission factor range	0.14–0.44	
Temperature (K)	295	295
No. of observed reflections (<i>I</i> > 2.5 σ (<i>I</i>))	5263	3306
<i>R</i>	0.045	0.055
<i>R</i> _w	0.054	0.081
$w = 1/(\sigma^2(F) + 0.001F^2)$; $\Delta = \ F_o - F_c\ $; $R = (\Sigma \Delta / \Sigma F_o)$; $R_w = (\Sigma w \Delta^2 / \Sigma w F_o^2)^{1/2}$		

are also accessible via reactions of [M₂Cl₂(cod)₂] with Li[CH(P(S)Ph₂)₂]. Reactions of the neutral complexes, [M(cod){CR(P(S)Ph₂)₂-S,S}], with HBF₄ resulted in immediate reprotonation with reformation of the cations, [M(cod){CHR(P(S)Ph₂)₂-S,S}]⁺.

The structures [Ir(cod){CH(P(S)Ph₂)₂-S,S}] and [Rh(cod){CH(P(S)Ph₂)₂-S,S}], as established by X-ray diffraction study, are shown as ORTEP diagrams in Figs. 1 and 2, respectively. Unit cell and other parameters related to the crystal structure determinations are in Table 1, fractional atomic coordinates in Tables 2 and 3, selected bond lengths in Table 4, and selected bond angles in Table 5 [35*]. Both structures consist of puckered 6-membered rings formed by coordination of the disulfide ligands via two sulfur atoms to the metal center. The rings lie in distorted boat conformations with the prows occupied by one sulfur and one phosphorus and the metal atoms in one side. For example, in the iridium complex, Ir(1), S(2), P(1), and C(0) are approximately coplanar with all four atoms less than 15 pm from the best least squares plane. The prows of the boat are P(2) and S(1), which lie respectively 73 and 116 pm from the least squares plane. In both complexes, bonding to two double bonds of a cod ligand completes approximate square planar coordination about the metal atoms.

* Reference number with asterisk indicates a note in the list of references

Discussion

^{31}P and ^{13}C NMR results are collected in Table 6 and the most significant bond lengths and angles are collected in Table 7. The bis(phosphine sulfide) ligands, $\text{CH}_2\{\text{P}(\text{S})\text{Ph}_2\}_2$ and $[\text{CH}\{\text{P}(\text{S})\text{Ph}_2\}_2]^-$, have not been studied by X-ray diffraction, so Table 7 includes data for the closely related tris(phosphine sulfide) species, $\text{CH}\{\text{P}(\text{S})\text{Ph}_2\}_3$ [36] and $[\text{C}\{\text{P}(\text{S})\text{Ph}_2\}_3]^-$ [37] in order to provide comparison data for bond lengths and angles in non-coordinated ligands.

Table 2

Fractional atomic coordinates and temperature parameters for $[\text{Ir}(\text{cod})(\text{CH}(\text{P}(\text{S})\text{Ph}_2)_2)]^a$

Atom	x	y	z	U_{eq}^b
Ir(1)	−14514(2)	17243(1)	24534(2)	324(1)
S(1)	−27134(15)	26376(10)	39631(16)	387(6)
S(2)	6063(13)	24003(10)	22375(16)	374(6)
P(1)	−23866(13)	23965(9)	58287(15)	315(5)
P(2)	4069(13)	33165(9)	35769(15)	312(5)
C(0)	−845(5)	2957(4)	5438(6)	37(2)
C(1)	−362(6)	1306(4)	438(7)	43(3)
C(2)	−706(7)	584(4)	1737(8)	48(3)
C(3)	−1774(8)	−312(5)	2277(10)	64(4)
C(4)	−3127(8)	−239(5)	3453(10)	64(4)
C(5)	−3271(6)	757(5)	3252(8)	51(3)
C(6)	−2986(6)	1391(5)	1847(8)	49(3)
C(7)	−2515(8)	1140(5)	283(9)	62(4)
C(8)	−1027(7)	1323(5)	−595(8)	58(3)
C(11)	−3645(5)	2746(4)	7339(6)	37(2)
C(12)	−3345(7)	3113(4)	8376(7)	48(3)
C(13)	−4353(8)	3342(5)	9592(8)	63(3)
C(14)	−5593(8)	3206(5)	9763(8)	64(3)
C(15)	−5892(7)	2865(6)	8697(9)	63(3)
C(16)	−4943(7)	2611(5)	7508(8)	54(3)
C(21)	−2659(5)	1156(4)	6612(6)	34(2)
C(22)	−3912(6)	587(4)	7645(8)	52(3)
C(23)	−4036(7)	−364(5)	8186(10)	63(3)
C(24)	−2943(8)	−742(5)	7654(8)	56(3)
C(25)	−1727(7)	−187(4)	6660(7)	51(3)
C(26)	−1571(6)	774(4)	6122(7)	44(3)
C(31)	1921(5)	3503(4)	3744(6)	36(2)
C(32)	2300(8)	2731(5)	4304(10)	60(4)
C(33)	3447(9)	2847(6)	4438(11)	74(5)
C(34)	4207(8)	3727(6)	4080(11)	75(4)
C(35)	3844(8)	4474(5)	3519(11)	73(4)
C(36)	2701(7)	4383(4)	3380(9)	53(3)
C(41)	429(6)	4421(4)	2461(6)	38(2)
C(42)	1342(7)	4759(5)	897(7)	53(3)
C(43)	1375(9)	5577(5)	53(9)	65(4)
C(44)	471(10)	6097(5)	781(10)	72(5)
C(45)	−450(10)	5763(5)	2346(11)	69(5)
C(46)	−450(8)	4922(4)	3192(9)	56(3)

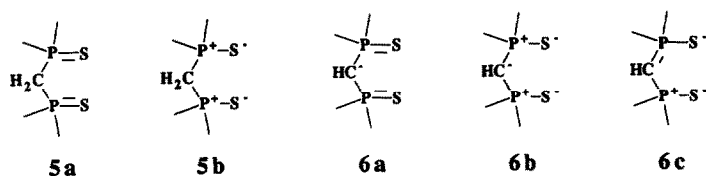
^a Estimated standard deviations are given in parentheses. Coordinates $\times 10^n$ where $n = 4$ for C, and 5 otherwise. Temperature parameters $\times 10^n$ where $n = 3$ for C, and 4 otherwise. ^b U_{eq} , the equivalent isotropic temperature parameter $U_{\text{eq}} = 1/3 \sum_i \Sigma_j U_{ij} a_i^* a_j^* (a_i \cdot a_j)$.

Table 3

Fractional atomic coordinates and temperature parameters for $[\text{Rh}(\text{cod})\{\text{CH}(\text{P}(\text{S})\text{Ph}_2)_2\}]^a$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^b
Rh(1)	14723(9)	17118(6)	25422(10)	289(5)
S(1)	−595(3)	23981(20)	2766(3)	333(18)
S(2)	2719(3)	26473(20)	1044(3)	353(19)
P(1)	−401(3)	33186(19)	1421(3)	281(19)
P(2)	2390(3)	24090(19)	−822(3)	280(18)
C(0)	843(10)	2978(7)	−427(12)	30(6)
C(1)	3321(11)	738(8)	1772(13)	39(8)
C(2)	3037(12)	1358(9)	3144(17)	51(10)
C(3)	2553(13)	1089(10)	4702(16)	57(10)
C(4)	1023(13)	1303(10)	5616(14)	52(10)
C(5)	355(11)	1262(8)	4580(14)	42(9)
C(6)	722(12)	550(8)	3218(14)	41(9)
C(7)	1794(13)	−341(8)	2696(18)	60(10)
C(8)	3136(13)	−247(9)	1543(16)	53(10)
C(11)	−434(11)	4423(7)	2558(13)	33(8)
C(12)	440(13)	4943(8)	1827(15)	47(10)
C(13)	433(16)	5795(9)	2725(18)	60(11)
C(14)	−502(17)	6116(9)	4279(20)	66(14)
C(15)	−1391(15)	5602(9)	4993(17)	57(11)
C(16)	−1363(12)	4741(8)	4133(14)	44(9)
C(21)	−1915(10)	3513(7)	1238(12)	30(8)
C(22)	−2666(12)	4396(8)	1586(15)	47(9)
C(23)	−3818(14)	4511(10)	1428(18)	66(11)
C(24)	−4231(14)	3745(10)	888(18)	67(13)
C(25)	−3426(15)	2855(10)	526(20)	71(13)
C(26)	−2288(12)	2738(9)	686(16)	51(10)
C(31)	3656(11)	2752(7)	−2359(12)	32(8)
C(32)	4935(12)	2632(9)	−2488(14)	44(9)
C(33)	5908(13)	2874(9)	−3703(16)	57(10)
C(34)	5616(13)	3213(9)	−4791(15)	53(10)
C(35)	4344(15)	3342(9)	−4644(15)	60(10)
C(36)	3356(12)	3115(8)	−3405(14)	44(9)
C(41)	2659(11)	1156(7)	−1602(13)	33(8)
C(42)	1574(11)	770(8)	−1104(14)	41(8)
C(43)	1714(12)	−179(8)	−1621(14)	46(9)
C(44)	2964(13)	−746(8)	−2674(16)	52(10)
C(45)	4029(13)	−366(9)	−3172(16)	52(10)
C(46)	3905(11)	588(8)	−2646(14)	43(8)

^a Estimated standard deviations are given in parentheses. Coordinates $\times 10^n$ where $n = 4$ for C, and 5 otherwise. Temperature parameters $\times 10^n$ where $n = 3$ for C, and 4 otherwise. ^b U_{eq} , the equivalent isotropic temperature parameter. $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i \cdot a_j)$.



Scheme 2. Some possible resonance structures of $\text{CH}(\text{P}(\text{S})\text{Ph}_2)_2$ and $[\text{CH}(\text{P}(\text{S})\text{Ph}_2)_2]^-$. Closely related resonance forms are also possible for complexes of these ligands.

Table 4

Selected interatomic distances (Å) ^a

[Ir(cod){CH(P(S)Ph ₂) ₂ }]		[Rh(cod){CH(P(S)Ph ₂) ₂ }]	
Atoms	Distance	Atoms	Distance
Ir(1)–S(1)	2.390(1)	Rh(1)–S(1)	2.374(3)
Ir(1)–S(2)	2.361(1)	Rh(1)–S(2)	2.397(3)
Ir(1)–C(1)	2.124(6)	Rh(1)–C(1)	2.162(11)
Ir(1)–C(2)	2.132(6)	Rh(1)–C(2)	2.162(12)
Ir(1)–C(5)	2.127(7)	Rh(1)–C(5)	2.168(11)
Ir(1)–C(6)	2.129(6)	Rh(1)–C(6)	2.147(11)
P(1)–S(1)	2.024(2)	P(1)–S(1)	2.055(4)
P(2)–S(2)	2.053(2)	P(2)–S(2)	2.016(4)
P(1)–C(0)	1.711(6)	P(1)–C(0)	1.705(11)
P(1)–C(11)	1.812(5)	P(1)–C(11)	1.822(11)
P(1)–C(21)	1.827(5)	P(1)–C(21)	1.825(11)
P(2)–C(0)	1.720(5)	P(2)–C(0)	1.722(11)
P(2)–C(31)	1.817(6)	P(2)–C(31)	1.822(11)
P(2)–C(41)	1.824(6)	P(2)–C(41)	1.838(11)
C(1)–C(2)	1.400(9)	C(1)–C(2)	1.381(19)
C(5)–C(6)	1.421(10)	C(5)–C(6)	1.423(18)

^a Estimated standard deviations are given in parentheses.

The effect of coordination on the NMR parameters of CH₂{P(S)Ph₂}₂ and [CH(P(S)Ph₂)₂][–] is relatively small (Table 6), as might be expected since the metal is attached at a site remote from the NMR active nuclei. The X-ray structural data (Table 7) shows that the main effect of coordination in both neutral and anionic ligands is a slight lengthening of the P–S bonds, consistent with an increase in the importance of resonance forms **5b** and **6b**, relative to **5a** and **6a** (Scheme 2). At the same time, the P–C bonds to the central carbon are slightly shortened, possibly due to additional polar contributions to the bond strengths in structures such as **5b** and **6b**. The alternative explanation involving P=C double bonds as in **6c** would apply only to the anionic ligands and is also less likely in view of the NMR data below.

Deprotonation of either free or coordinated CH₂{P(S)Ph₂}₂ results in two principal changes in the NMR: (a) shielding of the central carbon (Table 6, C_A) of the phosphine sulfide ligand is strongly increased, by 18.9 ppm (free ligand), 19.5 ppm (M = Rh) and 16.9 ppm (M = Ir); (b) the one-bond coupling (Table 6, ¹J(P–C_A)) from phosphorus to the central carbon is increased, from 45 to 110 Hz (free ligand), from 48 to 91 Hz (M = Rh) and from 46 to 95 Hz (M = Ir).

The increased shielding of C_A contrasts strongly with the effect of deprotonation on acetylacetonate, which results in deshielding of the central carbon, indicating development of a C=C double bond and delocalization of the negative charge onto oxygen in resonance forms analogous to **6c**. Thus the methine carbon of the deprotonated phosphine sulfides is much more negatively charged than that in acetylacetonate anion. This conclusion is also consistent with previous results on simple ylides, where structures involving a P=C double bond are considered less important than those involving some charge separation, P⁺–C[–], since the ¹³C NMR shifts are not deshielded as they are in alkenes [38].

Table 5

Selected bond angles (deg) ^a

[Ir(cod){CH(P(S)Ph ₂) ₂ }]		[Rh(cod){CH(P(S)Ph ₂) ₂ }]	
Atoms	Angle	Atoms	Angle
S(1)–Ir(1)–S(2)	97.8(1)	S(1)–Rh(1)–S(2)	97.4(1)
S(1)–Ir(1)–C(1)	157.5(2)	S(1)–Rh(1)–C(1)	161.0(3)
S(1)–Ir(1)–C(2)	162.4(2)	S(1)–Rh(1)–C(2)	160.6(4)
S(1)–Ir(1)–C(5)	86.3(2)	S(1)–Rh(1)–C(5)	85.8(3)
S(1)–Ir(1)–C(6)	87.8(2)	S(1)–Rh(1)–C(6)	89.4(3)
S(2)–Ir(1)–C(1)	86.1(2)	S(2)–Rh(1)–C(1)	87.0(3)
S(2)–Ir(1)–C(2)	89.7(2)	S(2)–Rh(1)–C(2)	88.1(4)
S(2)–Ir(1)–C(5)	159.6(2)	S(2)–Rh(1)–C(5)	158.1(3)
S(2)–Ir(1)–C(6)	160.3(2)	S(2)–Rh(1)–C(6)	162.1(3)
C(1)–Ir(1)–C(2)	38.4(2)	C(1)–Rh(1)–C(2)	37.3(5)
C(1)–Ir(1)–C(5)	97.7(2)	C(1)–Rh(1)–C(5)	97.0(4)
C(1)–Ir(1)–C(6)	81.8(2)	C(1)–Rh(1)–C(6)	81.5(5)
C(2)–Ir(1)–C(5)	81.3(3)	C(2)–Rh(1)–C(5)	82.4(5)
C(2)–Ir(1)–C(6)	90.4(2)	C(2)–Rh(1)–C(6)	90.9(5)
C(5)–Ir(1)–C(6)	39.0(3)	C(5)–Rh(1)–C(6)	38.5(5)
Ir(1)–S(1)–P(1)	102.1(1)	Rh(1)–S(1)–P(1)	110.8(1)
Ir(1)–S(2)–P(2)	110.7(1)	Rh(1)–S(2)–P(2)	102.0(1)
S(1)–P(1)–C(0)	112.7(2)	S(1)–P(1)–C(0)	117.8(4)
S(1)–P(1)–C(11)	107.5(2)	S(1)–P(1)–C(11)	107.1(4)
S(1)–P(1)–C(21)	110.6(2)	S(1)–P(1)–C(21)	105.6(4)
C(0)–P(1)–C(11)	111.3(3)	C(0)–P(1)–C(11)	114.2(5)
C(0)–P(1)–C(21)	110.0(3)	C(0)–P(1)–C(21)	105.7(5)
C(11)–P(1)–C(21)	104.5(2)	C(11)–P(1)–C(21)	105.4(5)
S(2)–P(2)–C(0)	117.3(2)	S(2)–P(2)–C(0)	112.6(4)
S(2)–P(2)–C(31)	104.9(2)	S(2)–P(2)–C(31)	107.9(4)
S(2)–P(2)–C(41)	107.5(2)	S(2)–P(2)–C(41)	110.2(4)
C(0)–P(2)–C(31)	105.8(3)	C(0)–P(2)–C(31)	111.3(5)
C(0)–P(2)–C(41)	114.5(3)	C(0)–P(2)–C(41)	110.2(5)
C(31)–P(2)–C(41)	105.8(3)	C(31)–P(2)–C(41)	104.3(5)
P(1)–C(0)–P(2)	120.8(3)	P(1)–C(0)–P(2)	120.8(6)
Ir(1)–C(1)–C(2)	71.1(3)	Rh(1)–C(1)–C(2)	71.3(7)
Ir(1)–C(2)–C(1)	70.5(3)	Rh(1)–C(2)–C(1)	71.4(7)
Ir(1)–C(5)–C(6)	70.6(4)	Rh(1)–C(5)–C(6)	69.9(6)
Ir(1)–C(6)–C(5)	70.4(4)	Rh(1)–C(6)–C(5)	71.5(6)

^a Estimated standard deviations are given in parentheses

The increase in $^1J(\text{P}-\text{C}_\text{A})$ on deprotonation is consistent with previous results on platinum complexes, **1**, where deprotonation to **3** produced increases in $^2J(\text{P}-\text{P})$ and $^2J(\text{Pt}-\text{P})$ as well as $^1J(\text{P}-\text{C}_\text{A})$ [24]. The increase is also consistent with changes in the structural parameters (Table 7). Thus, the P–C–P bond angle opens by about 5° on deprotonation, to almost exactly the trigonal angle of 120°, indicating a higher *s*-character at the central carbon. Also, deprotonation shortens the P–C bonds to the central carbon by about 10 pm. In view of the NMR shielding data, which indicates a relatively unimportant role for structures **6c**, this shortening may be attributed to increased ionic contributions in **6b** rather than to double bonds in **6c**. Also, as expected, if **6b** is more important in the deprotonated complexes (relative to **5b** in the protonated ones), the P–S bonds are slightly longer in the

Table 6

Phosphorus-31 and carbon-13 nuclear magnetic resonance parameters

Complex	Chemical shifts (ppm) ^a				Coupling constants (Hz) ^b		
	$\delta(P)$	$\delta(C_A)$	$\delta(C_B)$	$\delta(C_C)$	$J(RhP)$	$J(PC_A)$	$J(RhC_B)$
$CH_2\{P(S)Ph_2\}_2$ ^c	34.6(s)	38.8(t)				45	
$[CH\{P(S)Ph_2\}_2]^-$ ^d	38.6(s)	19.9(t)				110	
$CHMe\{P(S)Ph_2\}_2$ ^{c,e}	46.5(s)	41.1(t)				43	
$[Rh(cod)\{CH_2\{P(S)Ph_2\}_2\}]^+$ ^{c,f}	36.8(d)	32.9(t)	85.1(d)	31.1(s)	5	48	11
$[Ir(cod)\{CH_2\{P(S)Ph_2\}_2\}]^+$ ^{c,g}	32.6(s)	32.3(t)	70.2(s)	31.6(s)	—	46	—
$[Rh(cod)\{CHMe\{P(S)Ph_2\}_2\}]^+$ ^{c,g,h}	48.5(d)	31.0(t)	85.1(d)	31.2(s)	4	44	11
$[Rh(cod)\{CH\{P(S)Ph_2\}_2\}]^+$	36.0(d)	13.4(t)	81.3(d)	31.3(s)	5	91	12
$[Ir(cod)\{CH\{P(S)Ph_2\}_2\}]^+$	34.1(s)	15.4(t)	65.8(s)	32.0(s)	—	95	—
$[Rh(cod)\{CMe\{P(S)Ph_2\}_2\}]^{+j}$	39.3(d)	^k	81.7(d)	31.2(s)	3	^k	12

^a Chemical shifts (δ) are quoted relative to 85% H_3PO_4 and $Si(CH_3)_4$ for ^{31}P and ^{13}C , respectively. All shifts are positive. C_A is the central, methylene or methine carbon of the phosphine ligand. C_B and C_C are, respectively, the unsaturated and saturated carbons of the cod ligand. All complexes had additional ^{13}C resonances in the phenyl region about 130 ppm. ^b The two bond couplings, $^2J(RhC_C)$, were not resolved. ^c $CDCl_3$ solution. ^d Li^+ salt, d_8 tetrahydrofuran solution. ^e $\delta(CH_3)$ 12.6(s) ppm. ^f ClO_4^- salt. ^g BF_4^- salt. ^h $\delta(CH_3)$ 13.4(s) ppm. ⁱ C_6D_6 solution. ^j $\delta(CH_3)$ 16.5(t) ppm. ^k $^2J(PC)$ 5 Hz. ^k Not observed.

Table 7

Selected average bond lengths (pm) and average bond angles (deg)

Compound	M-S	M-C	P-S	P-C	S-M-S	M-S-P	S-P-C	P-C-P
$[CH\{P(S)Ph_2\}_3]^a$			194.4	188.3			112.5	115.3
$[C\{P(S)Ph_2\}_3]^-$ ^b			197.6	176.2		^c	119.9	
$[Rh(cod)\{CH_2\{P(S)Ph_2\}_2\}]^+$ ^d	241.0	213.8	199.8	182.5	98.8	104.5	110.7	114.6
$[Ir(cod)\{CH\{P(S)Ph_2\}_2\}]$	237.6	212.8	203.9	171.6	97.8	106.4	115.0	120.8
$[Rh(cod)\{CH\{P(S)Ph_2\}_2\}]$	238.5	216.0	203.5	171.4	97.4	106.4	115.2	120.8

^a Data from ref. 36. ^b Data from ref. 37. ^c Not available. ^d Data from ref. 20.

deprotonated complexes. Finally, we note that metal-sulfur bonds in the deprotonated complexes are slightly shorter, reflecting the fact that the formal S^- of structure **6b** is a better ligand than the uncharged sulfur of **6a**.

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