40904-67-4; [C_7H_7MoCO(phosars)]$^+PF_6^-$, 40832-27-7; [C_7H_7MoCO(mdiphos)]$^+PF_6^-$, 40832-28-8; C_7H_7MoCO(pyphos)I, 40832-29-9; [C_7H_7MoCO(pyhos)]$^+PF_6^-$, 40832-30-2; C_7H_7MoCO(distib)I, 39324-46-4; C_7H_7MoCO(triphos)I, 39322-77-5; [C_7H_7Mo(triphos)]$^+I^-$, 39322-76-4; [C_7H_7Mo(triphos)]$^+PF_6^-$, 40832-31-3; C_7H_7Mo(diphos)I, 39322-74-2; C_7H_7Mo(phosars)I, 39322-73-1; C_7H_7Mo(arsars)I, 39322-72-0; $C_7H_7MoC_{12}H_8$·N_2I, 40832-32-4; $C_7H_7MoC_{10}H_8N_2I$, 40832-33-5; diphos, 1663-45-2; *cis*-diphos, 983-80-2; phosars, 23582-06-1; mdiphos, 23936-60-9; triphos, 22031-12-5; pyphos, 10150-27-3; distib, 30224-53-4; $C_7H_7Mo(CO)_2I$, 36580-34-4.

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Murray Hill, New Jersey 07974

Ortho Phenyl Hydrogen Interactions in Bis[1,2-bis(diphenylphosphino)ethane]-Metal Complexes

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The ^{1}H nmr spectra at 30° of the complexes [Ir(dppe)$_2X_2$]Cl ($X_2 = O_2, S_2, Se_2$), *cis*-[M(dppe)$_2$(CO)$_2$] (M = Cr, Mo, W), [Ir(dppe)$_2C_3S_2$]Cl, and *cis*-[Ru(dppe)$_2$(CH_3)Cl] (dppe = 1,2-bis(diphenylphosphino)ethane) all show a 1:2:1 triplet of intensity 4 protons or, in the case of the last two complexes, two triplets each of intensity 2 protons in the range τ 3.5–4.3. From the decoupling behavior and temperature dependence of the triplets, together with the known X-ray structure of [Ir(dppe)$_2S_2$]Cl, it is shown that they are due to the resonance of certain ortho phenyl hydrogen atoms shifted upfield from the main phenyl multiplet by interaction with the two nonphosphorus cis groups. It is suggested that the presence of such a triplet in the spectrum of a six-coordinate bis(dppe) complex is conclusive evidence for cis geometry, but its absence is only tentative evidence for trans geometry.

Introduction

A recent X-ray structure determination[1] on the complex [Ir(dppe)$_2S_2$]Cl [dppe = 1,2-bis(diphenylphosphino)ethane] has shown that two ortho phenyl hydrogen atoms are, respectively, 2.54 and 2.57 Å distant from the sulfur atoms, while no other S· · ·H contact in the cation is less than 2.8 Å. It was suggested that there might be a significant interaction between the S_2 ligand and the two closest hydrogens. In this paper we report proton nmr evidence for such an interaction and show that it is present in all of the complexes [Ir(dppe)$_2X_2$]Cl ($X_2 = O_2$, S_2, and Se_2) as well as [Ir(dppe)$_2C_3S_2$]Cl, *cis*-[Ru(dppe)$_2$(CH_3)Cl], and *cis*-[M(dppe)$_2$(CO)$_2$] (M = Cr, Mo, and W). Furthermore, we find no evidence of ortho phenyl hydrogen interactions in trans isomers of [M(dppe)$_2$XY] (M = Ir, X = Y = I; M = Ru or Os, X = Y = Cl). Our results therefore suggest a convenient method of distinguishing cis and trans isomers of [M(dppe)$_2$XY] complexes.

Although the hydrogen-cis-ligand interactions elucidated in the present work exert an important effect on the phenyl region ^{1}H nmr spectrum, they are much weaker than the ortho phenyl hydrogen-metal interactions found in a number of tertiary phosphine-metal complexes.[2] In particular, there is no evidence of internal addition to the cis ligand or of deuterium exchange with the phenyl hydrogen atoms.

Experimental Section

The following compounds were prepared by the procedure in the reference cited: [Ir(dppe)$_2$]Cl,[3] [Ir(dppe)$_2$CO]Cl,[3] [Ir(dppe)$_2O_2$]Cl,[3] [Ir(dppe)$_2S_2$]Cl,[4] [Ir(dppe)$_2Se_2$]Cl,[4] [Ir(dppe)$_2C_3S_2$]Cl,[5] *cis*-[Ru(dppe)$_2$(CH_3)Cl],[6] *cis*-[M(dppe)$_2$(CO)$_2$] (M = Cr, Mo, W),[7] *trans*-[Cr(dppe)$_2$(CO)$_2$],[7] *trans*-[M(dppe)$_2Cl_2$] (M = Ru, Os).[8] The identity of the products was confirmed by ir spectroscopy and melting point determinations and, where necessary, by microanalysis.

***trans*-[Ir(dppe)$_2I_2$]Cl** was prepared by adding dropwise a solution of I_2 (49.5 mg, 0.195 mmol) in methylene chloride (25 ml) to [Ir(dppe)$_2$]Cl (200 mg, 0.195 mmol) in degassed methylene chloride (15 ml) under N_2. After 2 hr ~100 ml of ether was added to give an orange-yellow precipitate. The product was collected, washed with ether, and dried *in vacuo*, yield 0.20 g (80%). *Anal.* Calcd for $C_{52}H_{48}ClI_2IrP_4$: C, 48.86; H, 3.78; Cl, 2.77; I, 19.86; P, 9.69. Found: C, 48.81; H, 4.25; Cl, 2.65; I, 20.72; P, 9.05. Conductivity measurements over the concentration range 5×10^{-3}–10^{-4} *N* in acetonitrile solution at 25.0 ± 0.1° confirm the formulation as a 1:1 electrolyte; Λ *vs.* $\sqrt{C}$ gave a linear plot with an intercept $\Lambda_0 = 141$ and a slope $A = 406$ (calcd, 334). Infrared spectra in the range 4000–250 cm^{-1} (CsI disk) showed only bands due to dppe, consistent with Cl^- being the anion. The ^{31}P nmr spectrum of [Ir(dppe)$_2I_2$]Cl was obtained on a Varian HA-100 at 40.5 MHz with broad-band proton decoupling. The sample, a concentrated solution of the complex in methylene chloride, was in a 5-mm o.d. nmr tube fitted with a coaxial capillary containing 85% H_3PO_4. A search to 8000 Hz on both sides of the phosphoric acid line revealed only a single absorption at δ +6.74 ppm. This supports the assignment of trans geometry to [Ir(dppe)$_2I_2$]Cl.

^{1}H nmr spectra were determined at 100 MHz with a Varian HA-100 spectrometer and, where necessary, at 300 MHz on an HR-300 machine. On the HA-100, temperatures were measured with a copper-constantan thermocouple; on the HR-300 the temperature was determined from the separation of the CH_3 and OH resonances in spectra of methanol, according to the calibration chart in the Varian manual. ^{31}P–^{1}H decoupling of the HA-100 spectra was accomplished by irradiating the sample at a nominal frequency of 40.5 MHz with a stabilized Model SD-60 NMR Specialties heteronuclear spin decoupler.

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Table I. Ortho Phenyl Hydrogen Nmr Shifts in Bis(1,2-bis(diphenylphosphino)ethane)-Metal Complexes

	$T = 30°$				$T = -120°$	
Complex	τ	Intensity^a	J_{P-H}, Hz	J_{H-H}, Hz	τ	Intensity^a
$[Ir(dppe)_2S_2]Cl^b$	3.89^f	3.6	9	8	4.98^h	2.0
$[Ir(dppe)_2O_2]Cl^b$	3.67^f	3.8	9	8	5.12^h	1.8
$[Ir(dppe)_2Se_2]Cl^b$	3.82^f	3.9	8	8	4.3^h	i
$[Ir(dppe)_2C_3S_2]Cl^c$	$3.48^{f,g}$	1.9	9	8		
	$4.31^{f,g}$	2.2	9	8		
cis-$[Ru(dppe)_2(CH_3)Cl]^d$	$3.62^{f,k}$	2.1	8			
	4.05^f	2.1	8	7	$4.71^{f,j}$	2.1
cis-$[W(dppe)_2(CO)_2]^e$	3.79^f	3.9	8	8		
cis-$[Mo(dppe)_2(CO)_2]^e$	3.83^f	4.0	8	8		
cis-$[Cr(dppe)_2(CO)_2]^e$	3.70^f	3.5	8	8		

[a] Number of protons; determined from intensity = 8(area under triplet/area under CH_2CH_2 absorption) and 40[area under triplet/(area under triplet + area under main phenyl multiplet)]. [b] In CD_2Cl_2 + ~14% CF_2Cl_2. [c] In CD_3CN. [d] In deuterated tetrahydrofuran. [e] In $CDCl_3$. [f] 1:2:1 triplet. [g] At −26°; this compound decomposes in solution at 30°. [h] Broad, structureless. [i] Could not be measured because of interference by solvent $CHDCl_2$ peak. [j] At −103°. [k] 300-MHz spectrum; not resolved at 100 MHz.

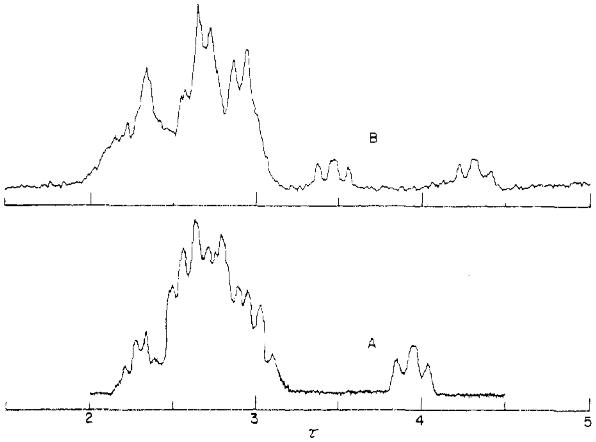


Figure 1. The phenyl region ^1H nmr spectrum at 100 MHz of (A) $[Ir(dppe)_2S_2]Cl$ in $CDCl_3$ at 30° and (B) $[Ir(dppe)_2C_3S_2]Cl$ in CD_3CN at −26°.

Results

Figure 1A shows the phenyl region ^1H nmr spectrum of $[Ir(dppe)_2S_2]Cl$ in $CDCl_3$ at 30°. At τ 3.94 there is a 1:2:1 triplet of intensity corresponding to 4 protons while the main phenyl multiplet, centered at τ ~2.7, corresponds to 36 protons. A similar triplet of intensity 4, with a main phenyl multiplet of intensity 36, is also found in the spectra of the complexes $[Ir(dppe)_2O_2]Cl$, $[Ir(dppe)_2Se_2]Cl$, and *cis*-$[M(dppe)_2(CO)_2]$ (M = Cr, Mo, W). The shifts and measured intensities are given in Table I. In the case of $[Ir(dppe)_2C_3S_2]Cl$ and *cis*-$[Ru(dppe)_2(CH_3)Cl]$, instead of a single triplet of intensity 4 there are two triplets, each of intensity 2, together with a main phenyl multiplet of intensity 36; this is shown in Figure 1B for $[Ir(dppe)_2C_3S_2]Cl$. The τ 3.62 triplet (Table I) of the ruthenium complex cannot be distinguished in the 100-MHz spectrum, but at 300 MHz it is fully resolved from the main phenyl multiplet.

^{31}P-^1H heteronuclear spin decoupling collapses the triplets described above to doublets. The triplets are unaffected by irradiation frequencies other than that at which collapse to a doublet occurs. A single phosphorus atom must therefore be coupled to the protons giving the triplet resonance; the 1:2:1 triplet structure arises from partial overlap of a pair of doublets, each of which results from ^{31}P splitting of one member of the doublet seen in the decoupled spectrum. The separation between the central member and either end member of a triplet is therefore J_{P-H} (Table I). Since the triplet structure is the same at 100 and at 300 MHz, the separation between the two lines of the doublet in the decoupled spectra cannot be due to a chemical shift but must result from proton coupling. The doublet splittings are listed in Table I as J_{H-H}.

In the spectrum of $[Ir(dppe)_2C_3S_2]Cl$, each triplet collapses to a doublet at a different irradiation frequency. The protons which give the two triplets must therefore be coupled to nonequivalent phosphorus atoms. The relative chemical shift of the latter is $\delta = [(\nu_1 - \nu_2)/40.5] - \delta_H = 18.1$, where ν_1 and ν_2 are, respectively, the irradiation frequencies required to decouple the first and second triplets and δ_H is the shift of the first triplet with respect to the second. For *cis*-$[Ru(dppe)_2(CH_3)Cl]$, the τ 4.05 triplet has been decoupled in the 100-MHz spectrum, but this has not been done for the τ 3.62 triplet because of the lack of a decoupler for the HR-300 spectrometer.

A marked temperature dependence was found for the $[Ir(dppe)_2S_2]Cl$ triplet resonance. As the temperature is lowered the triplet moves to higher field and broadens; by about −90° it has completely collapsed and by −100° a new band has appeared at still higher field. At −120°, the lowest temperature studied, a limiting spectrum has not yet been achieved, and the new band, now at τ 4.98, is still broad and structureless; it has intensity corresponding to two protons. The triplet bands of intensity 4 in the $[Ir(dppe)_2O_2]Cl$ and $[Ir(dppe)_2Se_2]Cl$ spectra show a similar temperature dependence. The shifts and measured intensities at −120° are given in Table I.

A temperature dependence study on the 100-MHz spectrum of *cis*-$[Ru(dppe)_2(CH_3)Cl]$ gave less dramatic results. As the temperature was lowered the τ 4.05 triplet moved to higher field, and by −103°, the lowest temperature studied, it had reached τ 4.71 without collapsing; although broadened, its triplet structure was still visible. The τ 3.62 triplet could not be discerned in the 100-MHz spectrum even at −103°; a shift of τ ~0.3 upfield should have made it easily visible.

Examination of the ^1H nmr spectra of the following complexes gave no evidence for a triplet on the high-field side of the phenyl multiplet: $[Ir(dppe)_2]Cl$, $[Ir(dppe)_2CO]Cl$, *trans*-$[Ir(dppe)_2I_2]Cl$, and *trans*-$[M(dppe)_2Cl_2]$ (M = Ru, Os). The ^1H nmr spectrum of *trans*-$[Cr(dppe)_2(CO)_2]$ in $CDCl_3$ was identical with the spectrum obtained from a solution of the cis isomer, but this is due to isomerization. Thus, a chloroform (ethanol free) solution of *trans*-$[Cr(dppe)_2(CO)_2]$ gives, after a short time, the same infrared spectrum in the CO stretching region as a solution prepared from the cis isomer: $\nu(CO) = 1840$ (s), 1789 (s) cm^{-1}, consistent with cis geometry.

Finally, we mention that we were unable to prepare the complex *cis*-$[Os(dppe)_2Cl_2]$ described in ref 8, although the trans isomer described in the same paper was easily obtained. Repeated attempts failed to give a product with a satisfactory analysis or with the crystal form or solubility behavior described for the cis isomer. ^{1}H nmr spectra of the unknown products showed complex phenyl multiplets but gave no evidence of the triplet expected for the cis complex.

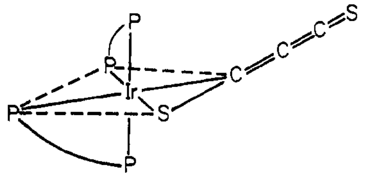
Discussion

The results in the preceeding section may be understood in terms of the structure of $[Ir(dppe)_2S_2]Cl$. Figure 2 is a drawing of the complex cation as given by Bonds and Ibers.[1] H(2) on ring 3 (3 H(2)) and H(6) on ring 6 (6 H(6)) are calculated to be 2.57 and 2.54 Å from S(2) and S(1), respectively, and it has been suggested that there may be an interaction between these hydrogen atoms and the sulfur atoms.[1] In solution rapid rotation of the phenyl rings can make the time-average environment on the nmr time scale the same for 3 H(2) and 3 H(6) and for 6 H(6) and 6 H(2). We assign the τ 3.9 triplet in the 30° spectrum of $[Ir(dppe)_2S_2]Cl$ to the four hydrogen atoms 3 H(2), 3 H(6), 6 H(2), and 6 H(6). The relatively close approach of these atoms to S(1) and S(2) apparently permits a weak interaction which shifts their resonance upfield from the main phenyl multiplet. Each of the four ortho hydrogen atoms is coupled by J_{H-H} to the adjacent meta hydrogen on the same ring and by J_{P-H} to the phosphorus atom to which the ring is attached; the two phosphorus atoms, P(2) and P(4), are equivalent as required by the observation of a single decoupling frequency.

The temperature dependence of the triplet shift in $[Ir(dppe)_2S_2]Cl$ confirms that rapid rotation of the phenyl rings is taking place.[9] As the temperature is lowered the triplet shift increases due to increasing concentration of the conformer with 3 H(2) and 6 H(6) close to S(2) and S(1) (Figure 2), at the expense of less stable conformers in which the ortho hydrogen atoms of rings 3 and 6 are not close to S(2) and S(1). Below $\sim -90°$ the rate of ring rotation has slowed sufficiently that the signal from 3 H(2) and 6 H(6) is no longer coalesced with the signal from 3 H(6) and 6 H(2). At $-120°$ the τ 4.98 band of intensity 2 is attributed to 3 H(2) and 6 H(6) in the conformer of Figure 2; the resonance from 3 H(6) and 6 H(2) is at lower fields, overlapped with other phenyl hydrogen absorptions. This separation of the ortho hydrogen resonances shows that the upfield shift must be due to an interaction with the environment and is not an effect transmitted *via* the C-H bond.

Since the other complexes in Table I have 1:2:1 triplets of the type found for $(Ir(dppe)_2S_2]Cl$, their stable conformation is inferred to have the protons analogous to 3 H(2) and 6 H(6) close to and interacting with the nonphosphine cis ligands. For $[Ir(dppe)_2O_2]Cl$ an X-ray structure determination[10] leads to 2.42 and 2.57 Å for the appropriate H· · ·O distances in the solid.

In two of the complexes in Table I, $[Ir(dppe)_2C_3S_2]Cl$ and *cis*-$[Ru(dppe)_2(CH_3)Cl]$, the phosphorus atoms analogous to P(2) and P(4) of Figure 2 are nonequivalent. For the carbon subsulfide complex, the idealized structure of which is believed to be



the shift between these two phosphorus atoms (one trans to C the other trans to S) was found to be 18.1 ppm. Two 1:2:1 intensity 2 triplets are found in the proton spectra of these compounds because the rings bearing the interacting ortho hydrogen atoms are linked to nonequivalent phosphorus atoms, in addition to the difference in the interaction of the two pairs of hydrogen atoms with the cis groups.

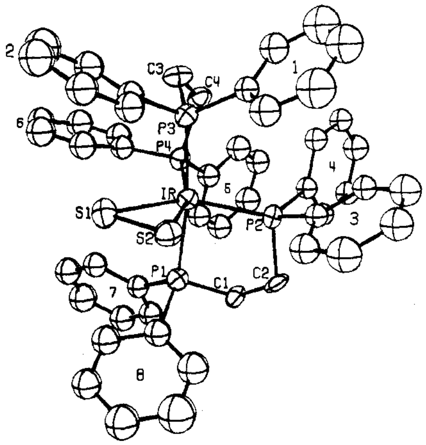


Figure 2. The structure of $[Ir(dppe)_2S_2]^+$ according to Bonds and Ibers.[1]

We suggest that in dealing with six-coordinate bis(dppe) complexes of uncertain stereochemistry, the presence in the ^{1}H nmr spectrum of a 1:2:1 triplet of the type described may be taken as conclusive evidence for cis geometry. The absence of such a triplet points to trans geometry but is not conclusive since, as evidenced by the near overlap of one of the triplets of *cis*-$[Ru(dppe)_2(CH_3)Cl]$ with the phenyl multiplet, the interaction with a cis group can sometimes be insufficient to shift the triplet out of the phenyl multiplet.

Registry No. I_2, 7553-56-2; $[Ir(dppe)_2]Cl$, 15390-38-2; *trans*-$[Ir(dppe)_2I_2]Cl$, 40635-58-3; $[Ir(dppe)_2S_2]Cl$, 40603-50-7; $[Ir(dppe)_2O_2]Cl$, 40603-52-9; $[Ir(dppe)_2Se_2]Cl$, 40603-51-8; $[Ir(dppe)_2C_3S_2]Cl$, 40635-59-4; *cis*-$[Ru(dppe)_2(CH_3)Cl]$, 40633-53-2; *cis*-$[W(dppe)_2(CO)_2]$, 17523-43-2; *cis*-$[Mo(dppe)_2(CO)_2]$, 17523-42-1; *cis*-$[Cr(dppe)_2(CO)_2]$, 40603-55-2.

Acknowledgment. We thank Professor J. A. Ibers for Figure 2 and Drs. F. A. Bovey and D. J. Patel for allowing us to use the HR-300 spectrometer.

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[9] See, for example, J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 381.

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