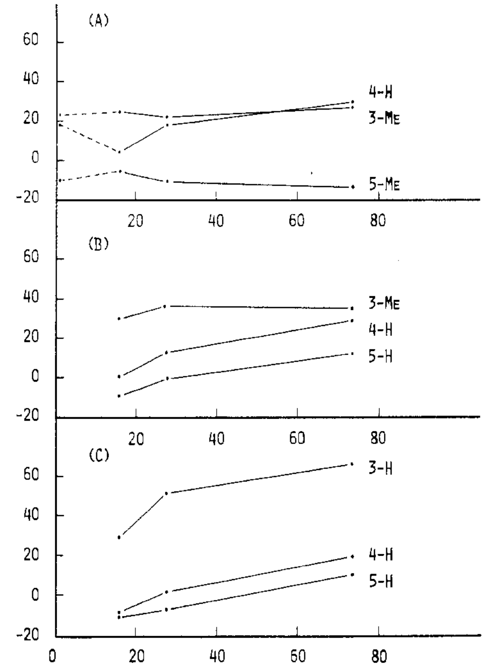

Figure 1. Comparison of dihydrobis(1-pyrazolyl)borate chelation shifts. Chelation shift ($\delta_{\text{K salt}} - \delta_{\text{Ni chelate}}$), Hz (ordinate) vs. $\Delta\epsilon$(K salt − Ni chelate) (abscissa). (A) $KH_2B(Me_2pz)_2$ (B) $KH_2B(Mepz)_2$, (C) $KH_2B(pz)_2$ in D_2O, MeOH, and Me_2CO; all nickel(II) chelates in $CDCl_3$. $KH_2B(Me_2pz)_2$ data also obtained in $CDCl_3$.

trimethylgermyl[16] groups in substituted pyrazoles has been reported at temperatures above 100°

Experimental Section

Potassium dihydrobis(1-pyrazolyl)borate and potassium dihydrobis[3,5-dimethyl(1-pyrazolyl)]borate were prepared by published procedures.[1,17] Potassium dihydrobis[3-methyl(1-pyrazolyl)]borate[18] was obtained by heating 26.3 g (0.32 mol) of 3(5)-methylpyrazole with 4.3 g (0.08 mol) of KBH_4 at 110° for 3 hr. A 45% yield of product was obtained with a mp of 204–206° after recrystallization from anisole.

Nickel(II) chelates were prepared by mixing nickel(II) chloride with excess ligand in water. Precipitates were air dried and recrystallized from methylcyclohexane (or benzene) after passing the solution through an aluminum oxide column. Solutions for ^1H NMR examination were obtained by ultrasonic agitation of 5–10 mg samples in 0.50 ml of deuterated solvent. Undissolved particles were removed by filtration and the solution was collected in a clean, 5 mm, NMR tube. Chloroform-*d* was passed through a 5 cm column of dry calcium carbonate immediately before use to remove impurities.

All ^1H NMR spectra at 90 MHz were obtained at 25° with a Brüker HFX-11 spectrometer equipped with a Fabritek 1074 time averaging computer. With organic solvents, 0.025 ml of tetramethylsilane was used as internal lock; in D_2O, sodium disilapentane sulfonate was employed as internal reference. Data in methanol-d_4 were recorded at 60 MHz and 30° using a Perkin-Elmer R-12B spectrometer. Standard deviations of ±0.4 and ±0.7 Hz were secured in the measurement of resonance frequencies of potassium salts and nickel(II) chelates, respectively.

Acknowledgment. The author expresses thanks to the National Bureau of Standards, Gaithersburg, Md. for a research fellowship (1971) and to Bruce Coxon for instruction in high resolution NMR. Appreciation is also extended to Clarisse L. Habraken and David L. Dalrymple for helpful discussions.

Registry No. $KH_2B(pz)_2$, 18583-59-0; $Ni[H_2B(pz)_2]_2$, 18131-13-0; $KH_2B(Mepz)_2$, 55701-51-4; $Ni[H_2B(Mepz)_2]_2$, 55701-52-5; $KH_2B(Me_2pz)_2$, 53241-68-2; $Ni[H_2B(Me_2pz)_2]_2$, 55722-67-3.

References and Notes

(1) S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3170 (1967).
(2) J. R. Jezorek and W. H. McCurdy, Jr., *Inorg. Chem.*, **14**, 1939 (1975).
(3) D. R. Wilkinson, Ph.D. Thesis, University of Delaware, 1972.
(4) J. Elguero and R. Jacquier, *J. Chim. Phys., Phys. Chim. Biol.*, **63**, 1242 (1966).
(5) J. Elguero, R. Jacquier, and H. C. N. Tien Duc, *Bull. Soc. Chim. Fr.*, 3727 (1966).
(6) H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **13**, 1291 (1974).
(7) S. Trofimenko, *Inorg. Chem.*, **9**, 2493 (1970).
(8) S. Trofimenko, private communication.
(9) D. R. Eaton and W. D. Phillips, *Adv. Magn. Reson.*, **1**, 103 (1965).
(10) P. S. Zacharias and A. Chakravorty, *Inorg. Nucl. Chem. Lett.*, **8**, 203 (1972).
(11) E. E. Zaev, V. K. Voronov, M. B. Shvartsberg, S. F. Vasilevsky, Yu. N. Molin, and I. L. Kotljarevsky, *Tetrahedron Lett.*, **5**, 617 (1968).
(12) D. Nicholls in "Comprehensive Inorganic Chemistry", Vol. 3, J. C. Bailar, H. J. Emeléus, R. Nyholm, and A. F. Trotman-Dickenson, Ed., Pergamon Press, New York, N.Y., 1973, p 1147.
(13) L. G. Tensmeyer and C. Ainsworth, *J. Org. Chem.*, **31**, 1878 (1966).
(14) R. Mathur and R. B. Martin, *J. Phys. Chem.*, **69**, 688 (1965).
(15) D. H. O'Brien and C. P. Hrung, *J. Organomet. Chem.*, **27**, 185 (1971).
(16) F. A. Cotton and D. J. Ciappenelli, *Synth. Inorg. Met. Org. Chem.*, **2**, 197 (1972).
(17) S. Trofimenko, *Inorg. Chem.*, **9**, 2493 (1970).
(18) This compound was first prepared by Sylvan Hersh who kindly supplied the procedure and analytical data. Calcd for $KC_8H_{12}N_4B$: C, 44.87; H, 5.65; N, 26.17. Found: C, 44.46; H, 5.50; N, 25.90. Infrared and NMR spectra are similar to other dihydrobis(1-pyrazolyl)borates. Bis chelates of dihydrobis[3-methyl(1-pyrazolyl)]borate with nickel(II), cobalt(II), copper(II), and zinc(II) were obtained by direct mixing of reagents in water. The products after recrystallization from ligroin or heptane yielded CHN analysis within 0.3% of theory. Results on the nickel(II) chelate are pertinent to this investigation. Calcd for $NiC_{16}H_{24}N_8B_2$: C, 47.02; H, 5.92; N, 27.41; Ni, 14.36. Found: C, 47.05; H, 6.07; N, 27.35; Ni, 13.98.

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Synthesis and Characterization of Bis(diphenylglyoximato) Complexes of Platinum

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Upon reviewing the critical features necessary for a new material to exhibit unusual electrical properties[1b] arising from intermolecular interactions in the solid, two prominent features surface: namely, partial oxidation of the metal and close intermolecular spacings.[1–6] The larger spatial extent of the $5d_{z^2}$ orbital of Ir^I and Pt^{II} than the first- and second-row congeners allows these metals to form in some cases partially oxidized one-dimensional complexes which exhibit unusual anisotropic physical properties, e.g., high dc conductivity.

In 1950 Edelman reported on the oxidation of bis(diphenylglyoximato)nickel(II), $Ni(HDPG)_2$, with bromine and iodine forming a formally trivalent nickel complex, $Ni(HDPG)_2X$, X = Br, I.[7] Subsequently, such reactions were effected on the palladium analogs.[8,9] Preliminary data indicate that upon oxidation the metal–metal distance decreases by 0.19–0.27 Å[8] and the dc conductivity increases by 5 orders of magnitude.[8,10] Because of these observations and because platinum exhibits a greater spatial extension of the d_{z^2} orbital than either the second- or the first-row congeners, metal–metal overlap and stronger intermolecular interactions occur to form more pronounced anisotropic properties.[1–6] For these reasons it seemed appropriate to investigate the chemistry of bis(diphenylglyoximato)platinum(II).[11]

Experimental Section

Physical Measurements. Electronic spectra were recorded on a Cary 15 spectrometer and infrared spectra were taken with a Beckman

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Table I. Chemical Analysis and Molecular Weight Data for Various Complexes of Platinum

	C		H		N		X		Mol wt		
Complex	Calcd[a]	Found	Calcd[a]	Found	Calcd[a]	Found	Calcd[a]	Found	Calcd[b]	*m/e*	Soln[c]
$Pt^{II}(HDPG)_2$	49.93	49.95	3.29	3.28	28.96	28.62			673	673	
$Pt^{IV}(HDPG)_2Cl_2$	45.17	44.66	2.98	2.92	7.53	7.35	9.52	9.36	743	743	784
$Pt^{IV}(HDPG)_2Br_2$	40.35	40.35	2.66	3.04			19.18	19.12	833	833	
$Pt^{IV}(HDPG)_2I_2$	36.26	36.37	2.39	2.27			27.37	26.72	927		
$Pt^{IV}(HDPG)_2(SCN)_2$	45.66	45.23	2.80	2.85	10.64	10.46			789		820

[a] Reference 14. [b] ^{195}Pt. [c] $CHCl_3$.

Table II. Unit Cell Parameters for Orthorhombic $M(HDPG)_2$

	Ni[a,b]	Ni[c]	Pd[c]	Pt[c]
a, Å	22.348 (4)	22.36	22.64	22.73
b, Å	15.177 (4)	15.20	15.35	15.40
c, Å	7.095 (2)	7.11	7.03	6.99
M–M, Å	3.547	3.55	3.52	3.50

[a] $Z = 4$ (4 molecules/unit cell); space group of *Ibam* or *Iba*2. [b] Lattice constants obtained by least-squares refinement of the setting angles for 12 high-angle reflections of a single crystal mounted in a FACS-I diffractometer equipped with a Mo tube and a graphite monochromator (λ 0.709261 Å). [c] Obtained from the least-squares refinement of the data in Table III.

IR-12 spectrometer calibrated against gaseous carbon monoxide. X-Ray powder data were recorded on a Philips diffractometer with monochromatic Cu radiation (λ 1.5418 Å). Intensities were based on peak heights at the diffraction maxima. Mass spectral analysis was performed by Schrader Analytical. The chemical analyses as obtained from Galbraith Laboratories are tabulated in Table I.

Bis(diphenylglyoximato)platinum(II), $Pt^{II}(HDPG)_2$. A hot filtered ethanol solution of 1.32 g of a mixture of *cis*- and *trans*-$Pt(SEt_2)_2Cl_2$[12] (2.96 mmol) and 1.42 g of diphenylglyoxime (5.92 mmol) was heated under reflux for 48 hr and then cooled to 0° to give a deep red product which was collected by filtration and recrystallization from *o*-dichlorobenzene; yield 510 mg (0.76 mmol; 26%).

Bis(diphenylglyoximato)dibromoplatinum(IV), $Pt^{IV}(HDPG)_2Br_2$. To a slurry of 325 mg of bis(diphenylglyoximato)platinum(II) (0.483 mmol) in 20 ml of dichloromethane was added 10 ml of 0.055 *M* bromine (in dichloromethane). The slurry was stirred until the solid dissolved. Then 20 ml of *n*-hexane was added and the dichloromethane was boiled off. Upon cooling, yellow crystals separated. Recrystallization was effected from *n*-hexane–dichloromethane; yield 310 mg (0.37 mmol; 77%).

After cooling to 0° for 12 hr of a warm solution of $Pt^{II}(HDPG)_2$ in *o*-dichlorobenzene to which 0.65 equiv of bromine (in *o*-dichlorobenzene) was added, crystals of both $Pt^{II}(HDPG)_2$ and $Pt^{IV}(HDPG)_2Br_2$ were collected and characterized by their mass spectrum.

$Pt^{IV}(HDPG)_2X_2$ (X = Cl, I, SCN). These complexes were prepared in a manner analogous to the preparation of the bromo complex with the use of the desired halogen or thiocyanogen[13] in dichloromethane. The thiocyanogen oxidation was carried out at −78° and warmed to room temperature.

Reaction of $Pt^{II}(HDPG)_2$ and $Pt^{IV}(HDPG)_2Br_2$. A filtered hot *o*-dichlorobenzene solution containing 69.69 mg of $Pt^{IV}(HDPG)_2Br_2$ (0.0837 mmol) and 56.28 mg of $Pt^{II}(HDPG)_2$ (0.0862 mmol) was allowed to stand at 0° for 12 hr. Upon filtration and drying a mixture of deep red needle and yellow prism crystals was deposited. The yellow crystals were extracted with dichloromethane; then, after filtration, *n*-hexane was added and the dichloromethane was boiled off yielding a yellow crystalline product. No black- or gold-colored phases were detected under the microscope. The red residue yielded 48 mg of $Pt^{II}(HDPG)_2$ (85%). From the extraction and recrystallization 57 mg of $Pt^{IV}(HDPG)_2Br_2$ (82%) was collected and characterized by mass spectra.

Results and Discussion

Divalent Platinum Complexes. Bis(diphenylglyoximato)platinum(II) forms deep red dichroic needle crystals which are isomorphous (as determined from X-ray powder data) with the Ni(II) and Pd(II) congeners and with bis(dimethylglyoximato)nickel(II), $Ni(HDMG)_2$.[15,16] The orthorhombic unit cell dimensions are listed in Table II and the indexed Bragg spacings are listed in Table III. Precession and Weissenberg photographs of a single crystal of $Ni(HDPG)_2$ showed systematic absences consistent with the space group *Iba*2 or *Ibam*. In accord with either space group $c/2$ is the metal–metal distance in the columnar chain. The Ni–Ni (3.549 Å) and Pd–Pd (3.52 Å) distances are in excellent agreement with the distances of 3.547 Å (Ni) and 3.517 Å (Pd) calculated from spectral data.[17] As typified by other square-planar congener group VIII complexes the Pt complex exhibits the shortest spacings even though the covalent radii go with the opposite trend.[1,6]

The large metal–metal spacings may be due to noncoplanar phenyl rings (resulting from steric interaction of ortho hydrogen atoms on adjacent phenyl groups). Consistent with the stronger metal–metal interaction for the Pt complex the solubility of the Pt complex is much lower in either dichloromethane or *o*-dichlorobenzene than are the solubilities of $Pd(HDPG)_2$ and $Ni(HDPG)_2$ complexes. This agrees with the results obtained for other bis(glyoximato)nickel triad complexes.[18]

The intermolecular interactions in the solid manifest a low-energy electronic transition. The low-energy absorbances for each of the nickel triad complexes account for the color of the complex in the solid state [red (Ni, 19,200 cm⁻¹; Pt, 17,950 cm⁻¹) and yellow (Pd, 22,475 cm⁻¹)] and are assigned to a charge-transfer absorption in accord with the $Ni(HDMG)_2$ complex.[19] These low-energy absorptions are not evident in solution, Table IV.

The room-temperature dc two probe polycrystalline conductivity of each of the $M(HDPG)_2$ (M = Ni, Pd, Pt) complexes is in the range of large gap semiconductors, i.e., $\sigma_{RT} < 10^{-10}$ ohm⁻¹ cm⁻¹. This is consistent with the filled band character of the complexes and the results obtained for $Ni(HDMG)_2$.[20]

Tetravalent Platinum Complexes. Oxidation of $Pt^{II}(HDPG)_2$ with halogen or thiocyanogen results in the formation of monomeric hexacoordinate Pt(IV) complexes, $Pt^{IV}(HDPG)_2X_2$, X = Cl, Br, I, SCN. These Pt^{IV} complexes were characterized by chemical analysis, molecular weight (Table I), and electronic spectra (Table IV). The electronic spectra indicate that the Pt^{IV} complexes are isoelectronic to each other. A trans geometry is assigned on the basis of a sharp singlet assigned to ν_{SCN} at 2130 cm⁻¹ in KBr for $Pt^{IV}(HDPG)_2(SCN)_2$. The two-probe polycrystalline dc conductivity of these Pt^{IV} complexes is less than 10^{-10} ohm⁻¹ cm⁻¹. This is consistent with filled molecular orbitals of these complexes and the lack of intermolecular interactions in the solid. Recently similar results were reported for the oxidation of bis(1,2-benzoquinone dioximato) complexes of the nickel(II) triad.[21]

Further attempts were made to prepare a formally trivalent platinum complex. Both oxidation of $Pt^{II}(HDPG)_2$ with less than 1 equiv of bromine and dissolution of equimolar amounts of $Pt^{II}(HDPG)_2$ and $Pt^{IV}(HDPG)_2Br_2$ in warm *o*-dichlorobenzene and cooling yield a mixture of the divalent and tetravalent complexes. No evidence was noted for the existence of a mixed-valent bis(diphenylglyoximato)platinum complex. Thus a structure of $M(HDPG)_2X$ comprised of alternating divalent and tetravalent platinum complexes (as observed for $Pt(NH_3)_2Br_3$[1a]) is unlikely.

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Registry No. $Pt^{II}(HDPG)_2$, 55660-52-1; $Pt^{IV}(HDPG)_2Br_2$, 55660-53-2; $Pt^{IV}(HDPG)_2Cl_2$, 55660-54-3; $Pt^{IV}(HDPG)_2I_2$, 55660-55-4; $Pt^{IV}(HDPG)_2(SCN)_2$, 55660-56-5; $Pt(SEt_2)_2Cl_2$, 14873-92-8.

Supplementary Material Available. Tables III and IV giving the indexed powder pattern data for $M(HDPG)_2$ (M = Ni, Pd, Pt) and the electronic absorption spectra of bis(diphenylglyoximato) complexes, respectively, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC50159E-9-75.

References and Notes

(1) (a) J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20**, 1 (1975); (b) J. S. Miller, *Adv. Chem. Ser.*, in press.
(2) K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969).
(3) H. R. Zeller, *Festkörperprobleme*, **13**, 31 (1973).
(4) E. B. Yagubskii and K. L. Khidekel, *Russ. Chem. Rev. (Engl. Transl.)*, **41**, 1011 (1972).
(5) I. F. Shchegolev, *Phys. Status Solidi A*, **12**, 9 (1972).
(6) T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, **1**, 99 (1972).
(7) L. E. Edelman, *J. Am. Chem. Soc.*, **72**, 5765 (1950).
(8) A. S. Foust and R. H. Soderberg, *J. Am. Chem. Soc.*, **89**, 5507 (1967).
(9) H. J. Keller and K. Seibold, *J. Am. Chem. Soc.*, **93**, 1309 (1971).
(10) A. E. Underhill, D. M. Watkins, and R. Pethig, *Inorg. Nucl. Chem. Lett.*, **9**, 1269 (1973).
(11) L. Chugaev, *Z. Anorg. Allg. Chem.*, **46**, 144 (1905).
(12) G. B. Kauffman and D. O. Cowan, *Inorg. Synth.*, **6**, 211 (1960).
(13) O. Glemser in "Handbook for Preparative Inorganic Chemistry," Vol. 1, G. Brauer, Ed., R. F. Riley, Translator, 2nd ed, Academic Press, New York, N.Y., 1962, p 67 ff, modified by the use of dichloromethane as solvent.
(14) J. S. Miller, *J. Chem. Educ.*, **50**, 431 (1973).
(15) L. E. Godycki and R. E. Rundle, *Acta Crystallogr.*, **6**, 487 (1953).
(16) D. E. Williams, G. Wohlauer, and R. E. Rundle, *J. Am. Chem. Soc.*, **81**, 755 (1959).
(17) C. V. Banks and D. W. Barnum, *J. Am. Chem. Soc.*, **80**, 4767 (1958).
(18) C. V. Banks and D. W. Barnum, *J. Am. Chem. Soc.*, **80**, 3579 (1958).
(19) Y. Ohashi, I. Hanazaki, and S. Nakakura, *Inorg. Chem.*, **9**, 2551 (1970); G. DeAlti, V. Galasso, and A. Bigotto, *Inorg. Chim. Acta*, **4**, 267 (1970).
(20) T. W. Thomas and A. E. Underhill, *Chem. Commun.*, 725 (1969).
(21) H. Endres, H. J. Keller, M. Mégnamisi-Bélombé, W. Moroni, and D. Nöthe, *Inorg. Nucl. Chem. Lett.*, **10**, 467 (1974).

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Mixed-Ligand Five-Coordinate Complexes of Iridium(I)

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Ligand substitution and addition reactions with $IrCOCl(PPh_3)_2$ have been widely studied and show a marked dependence on the identity of the attacking reagent. Carbon monoxide adds to form $Ir(CO)_2Cl(PPh_3)_2$,[1] while $PMePh_2$ gives the unsaturated substitution product $IrCOCl(PMePh_2)_2$;[2] excess $PMePh_2$ has no effect.[3] $IrCOCl(PMePh_2)_2$, in turn, reacts with tertiary phosphites, L', in the presence of $NaBPh_4$ to give $[IrCO(PMePh_2)_2L'_2]BPh_4$.[3] $IrCOCl(PMe_2Ph)_2$ reacts with equimolar PMe_2Ph to produce $IrCOCl(PMe_2Ph)_3$, which has an extremely long iridium–chlorine bond in the solid state.[4] Two moles of PMe_2Ph produce $IrCO(PMe_2Ph)_4^+$, excess CO yields $Ir(CO)_3(PMe_2Ph)_2^+$, and equimolar PMe_2Ph and CO yield $Ir(CO)_2(PMe_2Ph)_3^+$.[5] $IrCOCl(PPh_3)_2$ reacts with $HPPh_2$ to give $IrCO(PHPh_2)_4^+$,[6] but PPh_3 gives $IrCO(PPh_3)_3^+$ salts only after preliminary removal of halide with Ag^+.[7]

Table I. ^{31}P NMR Parameters[a]

	δ(phosphite)	δ(phosphine)	J_{PP}
$P(OCH_2)_3CCH_3$	91.5[b]		
$Ir[P(OCH_2)_3CCH_3]_5^+$	84.70		
$Ir[P(OCH_2)_3CCH_3]_4(PPh_3)^+$	83.65	+1.99	54.0
$Ir[P(OCH_2)_3CCH_3]_3(PPh_3)CO^+$	80.42	−1.43	92.0
$Ir[P(OCH_2)_3CCH_3]_4CO^+$	80.50		
$Ir[P(OCH_2)_3CCH_3]_3(PPh_3)_2^+$	79.22	−1.15	49.5
$Ir[P(OCH_2)_3CCH_3]_2(PPh_3)_2CO^+$	78.36	+.58	44.0
$IrCOCl(PPh_3)_2$		+23.5	
PPh_3		−5.4	

[a] In $CHCl_3$ at 30°. [b] M. Crutchfield, C. Dungan, J. Letcher, V. Mark, and J. Van Wazer, *Top. Phosphorus Chem.*, **5**, 267 (1967).

Although caged phosphite esters[8] such as $P(OCH_2)_3CR$ seem suited to forming highly substituted phosphite complexes, the reactions of these ligands with second and third row transition metals have been little studied. We report here the results of a study of the reactions of $IrCOCl(PPh_3)_2$ and $IrN_2Cl(PPh_3)_2$ with $P(OCH_2)_3CCH_3$. The interpretation[3] of "virtually coupled" proton NMR spectra of $Ir(CO)_x(PR_3)_{5-x}^+$ complexes is not possible without knowledge of phosphorus–phosphorus coupling constants in a trigonal bipyramid. Values of $^2J_{PP}$ are reported here and are found to lie in narrow ranges which appear to be structurally diagnostic. Stereochemical nonrigidity is established for a number of products.

Experimental Section

$IrCOCl(PPh_3)_2$,[9] $IrN_2Cl(PPh_3)_2$,[10] and $P(OCH_2)_3CCH_3$[8] were prepared according to literature methods. Fourier transform ^{31}P NMR spectra were recorded with white-noise proton decoupling as described earlier.[11] Downfield chemical shifts are recorded as positive. Reactions were run and samples prepared under N_2.

$IrP(OCH_2)_3CCH_3]_5Cl\cdot p$-Xylene. One millimole of $Ir(CO)Cl(PPh_3)_2$ and 5 mmol of $P(OCH_2)_3CCH_3$ were stirred and refluxed in *p*-xylene for 2 hr. The resulting slurry was cooled and filtered, and the precipitate was vacuum dried. The infrared spectrum showed no CO stretching vibration, and no vibrations characteristic of PPh_3. Proton NMR (in $CDCl_3$): δ 4.16 (CH_2), 0.77 (CH_3); peaks due to *p*-xylene are also present in the correct intensity ratios at δ 6.98 (CH) and 2.25 (CH_3). Anal. Calcd for $C_{33}H_{55}ClIrO_{15}P_5$: C, 36.88; H, 5.12. Found: C, 36.56; H, 5.15.

Other reactions were run by adding 10 ml of benzene to a degassed sample of 0.1 g of the iridium compound and the appropriate amount of $P(OCH_2)_3CCH_3$. Gas evolution was vigorous, even for an iridium:phosphite ratio of 1:2. White solid formed immediately, but the reaction was stirred for 2 hr at 25° before filtration and vacuum drying.

Results

IrN_2ClL_2 reacts with L' (mole ratio 1:4.5) in benzene at 25° to precipitate a white solid which shows vibrational frequencies characteristic of both L and L';[12] no bands due to coordinated N_2 are present. Phosphorus NMR shows the product to be a mixture of IrL'_5^+ and IrL'_4L^+ in a mole ratio 1:5. The former was identified by independent synthesis (see below). The formula of the latter is based on the appearance of an A_4X spectral pattern with J_{AX} = 54.0 Hz.

When the reaction of IrN_2ClL_2 with L' is carried out at a 1:4 mole ratio, dinitrogen is still completely displaced. The benzene-insoluble material contains a trace of IrL'_5^+, along with equal amounts of IrL'_4L^+ and $IrL'_3L_2^+$. The latter shows an A_3X_2 spectral pattern with J_{AX} = 49.5 Hz.

$IrCOClL_2$ reacts with L' (mole ratio 1:5) in refluxing *p*-xylene with precipitation of analytically pure $[IrL'_5]Cl\cdot C_8H_{10}$. The chemical shift of this cation is shown in Table I.