kinetics of their formation, because nickel(II) hydroxide would precipitate.

Comparison between the Three Ligands. We see from Table I that $\vec{k}_{\mathrm{Ni}}$ increases with increasing acid strength of the ligand. This trend is in the expected direction, since it is reasonable to assume that the stronger the acid, the weaker the internal hydrogen bond.

On the other hand, the values of $\overleftarrow{k}_{\mathrm{Ni}}$ differ only little from each other, whereas usually it is the rate of *dissociation* that is characteristic for the ligand[6] and thus determines the strength of the complex. In the present case, the opposite is true, and we get the somewhat unusual situation[30] where the formation constant is higher the stronger the acid.

Reaction between $NiOH^+$ and Ligands. Table I shows that $\vec{k}_{\mathrm{NiOH}}$ is much higher than $\vec{k}_{\mathrm{Ni}}$ and is almost uninfluenced by the acid strength of the ligand.

The reaction via HL* can be ruled out on the same grounds as before; it would require the rate constant for $NiOH^+$ to be several powers of 10 above the "normal" value for Ni^{2+}. There is no corroborating evidence for such a behavior. To our knowledge, the only paper where a kinetic influence of $NiOH^+$ is reported at all is that by Funahashi and Tanaka[13] which pertains to 4-(2-pyridylazo)resorcinol. There, k_{NiOH} is higher than k_{Ni} by a factor of not much more than 4. The authors ascribe the enhanced reactivity of $NiOH^+$ to the influence of OH^- on the rate of water loss from the inner hydration sphere, an effect which has been found to be very pronounced[6] in ions of the type of Fe(III).

We belive that, in the present case, the explanation must lie elsewhere; if the "normal" value of k_{NiOH} were really above that of k_{Ni}, the contribution of $NiOH^+$ to the observed rate of complexation should have made itself felt in other investigations carried out in a pH range similar to, or higher than, ours (see, e.g., ref 28). We suggest that it is only in those cases where the reaction site is blocked by a proton (internally hydrogen bonded or not; Funahashi and Tanaka concluded that there is little effect of hydrogen bonding in their case) that the reactivity of $NiOH^+$ exceeds that of the unhydrolyzed Ni^{2+}. The basic properties of the former substance will enable it to assist in the breakage of the hydrogen bond or in the total displacement of the proton. This would explain why the reactivity of $NiOH^+$ has so far almost universally escaped notice. As we have already noted, its reaction with a protonated ligand HL has the same pH dependence as that of Ni^{2+} with L^-. Except when HL is an extremely weak acid—such as the ligands employed in this work—the latter reaction path is dominant and may completely mask the contribution of $NiOH^+$.

Registry No. 4-(Phenylazo)resorcinol, 2051-85-6; tropaeolin O acid, 2050-34-2; 4-(*p*-nitrophenylazo)resorcinol, 74-39-5; 4-(*m*-nitrophenylazo)resorcinol, 2243-74-5; Ni^{2+}, 14701-22-5.

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Contribution from the Department of Chemistry,
University of Manchester Institute of Science and Technology,
Manchester M60 1QD, England

Platinum(II) Thiocyanate Complexes of Some Bidentate Group 5B Donor Ligands

R. J. Dickinson, W. Levason, C. A. McAuliffe,* and R. V. Parish*

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The thiocyanate ion is one of the most intensively studied ambidentate ligands,[1] but in spite of this a comprehensive explanation of the effects of neutral ligands on the nature of the M–CNS bond is still not possible (–CNS, coordination atom unspecified; –NCS, N bonded; –SCN, S bonded). Palladium(II) thiocyanate complexes of bidentate group 5B donor ligands have been thoroughly investigated,[2–7] and the type of thiocyanate coordination has been shown to depend both upon the ligand backbone "bite" and the nature of the group 5B donor atoms. Platinum(II) complexes have received less attention, but, since the covalent radii of Pd(II) and Pt(II) are the same (1.31 Å),[8] on steric grounds alone the same ligand should promote identical thiocyanate coordination to both metals. We have recently shown[5,6] that in the cases of (*o*-diphenylphosphinophenyl)diphenylstibine, *o*-$C_6H_4(PPh_2)(SbPh_2)$ (sbp), and *o*-phenylenebis(diphenylarsine), *o*-$C_6H_4(AsPh_2)_2$ (aa), the palladium(II) complexes are of the type PdL(NCS)(SCN), but the platinum analogues are $PtL(SCN)_2$. Here we report the results of a study of the platinum(II) complexes of group 5B donor bidentates with ethylene and alkane backbones.

Experimental Section

Physical measurements were made as described previously.[5] The following ligands were prepared by literature methods: bis(diphenylphosphino)methane (dpm),[9] 1,2-bis(diphenylphosphino)ethane (dpe),[9] 1,3-bis(diphenylphosphino)propane (dpp),[10] *cis*-1,2-bis(diphenylphosphino)ethylene (vpp),[11] 1,2-bis(diphenylarsino)ethane (dae),[12] *cis*-1,2-bis(diphenylarsino)ethylene (vaa),[13] 1-diphenylarsino-2-diphenylphosphinoethane (pae),[14] *cis*-1-diphenylarsino-2-diphenylphosphinoethylene (vpa).[14]

Pt(dpe)(NCS)(SCN). Sodium tetrachloroplatinate(II) (0.38 g, 1 mmol) and potassium thiocyanate (0.5 g, ~5 mmol) were stirred together in aqueous solution (20 cm^3) for 3 h. A solution of dpe (0.396 g, 1 mmol) in dichloromethane (10 cm^3) was added, followed by sufficient ethanol to produce a homogeneous solution, and the mixture was refluxed for 1 h. The solution was evaporated to dryness, and

Table I. Analytical and Infrared Data of the Complexes

Compd	% C		% H		% N		ν(CN), cm^{-1}		$\nu_{1/2}$, cm^{-1}	A/ CNS^{a,b}
	Found	Calcd	Found	Calcd	Found	Calcd	Nujol	Dichloromethane		
Pt(dpm)(SCN)$_2$	46.9	46.7	3.2	3.1	4.05	4.0	2125 sh	2118	12	3.8
							2120 sh	2085	26	8.2
Pt(dpe)(NCS)(SCN)	47.4	47.6	3.5	3.5	3.9	4.2	2130 sh	2120	9	2.6
							2095 br	2088	33	10.5
Pt(dpp)(NCS)(SCN)	48.1	47.6	3.5	3.4	3.9	3.8	2130 sh	2120	8	0.8
							2095 br	2092	38	12.1
Pt(vpp)(NCS)(SCN)	47.4	47.6	3.1	3.2	3.9	3.8	2115 sh	2124	105	2.1
							2080 br	2090	35	10.5
Pt(vpa)(NCS)(SCN)	44.7	44.8	3.0	2.9	3.7	3.5	2115 sh	2122	9	1.8
							2080 br	2090	33	9.3
Pt(vaa)(SCN)$_2$	42.2	42.0	2.8	3.0	3.5	3.5	2115 sh	2116	11	2.7
								2086	26	8.9
Pt(dae)(SCN)$_2$	42.1	41.8	3.0	3.2	3.4	3.2	2130 sh	2106	11	2.1
							2122 sh	2078	30	7.6
Pt(pae)(NCS)(SCN)	44.7	44.1	2.9	3.1	3.7	3.8	2110 sh	2116	14	2.3
							2090 br	2092	27	10.9
Pd(pae)(SCN)$_2$	50.6	50.3	3.6	3.5	4.2	4.1	2120 sh	2110	16	2.6
							2100 sh	2084	35	8.4

[a] $\times 10^{-4}$ cm^{-1} mol^{-1}. [b] We feel that integreated intensity values should be reported, though the reader should realize that these complexes are isomerizing while measurements are being taken.

the residue was dissolved in boiling *N,N*-dimethylformamide and reprecipitated with diethyl ether. Recrystallization from CH_2Cl_2–EtOH produced cream-colored crystals (70%). PtL(CNS)$_2$ complexes (L = dae, dpp, vpp, vpa, vaa, pae) were prepared similarly.

Pt(dpm)(SCN)$_2$. Dithiocyanotobis(benzonitrile)platinum(II) (0.517 g, 1 mmol) was dissolved in dichloromethane (20 cm^3) and dpm (0.395 g, 1 mmol) in dichloromethane (10 cm^3) was added; the mixture stirred under reflux for 1 h. Evaporation to small volume and recrystallization of the precipitate from CH_2Cl_2–EtOH produced cream-colored crystals (85%). PtL(CNS)$_2$ complexes (L = vpp, vpa, vaa) were prepared similarly.

Pd(pae)(SCN)$_2$ was prepared in a manner similar to the preparation of the platinum analogue from Na_2PdCl_4.

Results and Discussion

The PtL(CNS)$_2$ complexes (L = dpe, dae, dpp, vpp, vpa, vaa, pae) were prepared from Na_2PtCl_4 and L in the presence of excess KNCS in H_2O–EtOH–CH_2Cl_2, followed by dissolution in boiling *N,N*-dimethylformamide to rearrange the Magnus-type salts which formed initially. The complexes could also be obtained directly from Pt(PhCN)$_2$(SCN)$_2$ and L in dichloromethane. In each case the same type of thiocyanate coordination was found to be present irrespective of the preparative route, and, furthermore, heating the solid complexes at ~120 °C under nitrogen did not produce any isomerization, indicating that the forms reported here are the thermodynamically stable ones. The complexes are all nonelectrolytes in 10^{-3} M nitromethane or 1,2-dichloroethane, and their electronic spectra exhibited no absorptions below ~28 000 cm^{-1}, consistent with planar PtL(CNS)$_2$ compounds.[5]

The mode of thiocyanate coordination in the solid complexes was determined by observation of the ν(CN) frequencies: a sharp band at >2100 cm^{-1} denoting M–SCN and a broad absorption at <2100 cm^{-1} denoting M–NCS linkages. Although a few cases have been reported where a particular type of linkage gives rise to absorptions outside these ranges,[1] it is reasonable to apply these criteria to a closely related series such as the one here. The ν(CN) bandwidths for the M–SCN and M–NCS types appear to be a fairly reliable guide, also. In some complexes the observation of ν(CS) or δ(NCS) vibrations is possible, but with the ligands used here these are often masked by ligand absorptions. The electronic spectral criteria applied so successfully by Meek et al.[2] to their Pd(II) complexes cannot be used with the same degree of certainty with these Pt(II) derivatives since the "d–d" bands are hidden by or appear as ill-defined shoulders on intense charge-transfer bands.

On the basis of infrared measurements (Table I) in the solid state the PtL(SCN)$_2$ complexes (L = dpm, vaa, dae) contain only Pt–SCN linkages, while PtL(NCS)(SCN) (L = dpe, dpp, vpp, vpa, pae) contain both isothiocyanato and thiocyanato linkages. In dichloromethane solution the position of the ν(CN) frequencies and the half-band widths show that M–NCS and M–SCN linkages are present in all of the complexes, which is not unexpected since dichloromethane belongs to Burmeister's[15] group B solvents which promote M–NCS coordination.

Recalling the fact that Pd(II) and Pt(II) have the same covalent radii, it is interesting to compare the type of Pt–CNS and Pd–CNS linkages found for a particular ligand. It is found that dpe promotes M(dpe)(NCS)(SCN) and dpm, vaa, and dae promote ML(SCN)$_2$ for both metals. The Pd(dpp)(NCS)$_2$ complex differs from the Pt(dpp)(NCS)(SCN) species as the PdL(SCN)$_2$ complexes differ from PtL(NCS)(SCN) (L = vpp, vpa, pae). Thus, we find examples for a particular ligand where palladium(II) appears to favor N,N bonding more than N,S (e.g., dpp) and for others where the tendency to N,S coordination over S,S is greater for Pt(II) than for Pd(II) (e.g., vpp, vpa, pae). In solution in dichloromethane it would appear that varying amounts of M–NCS and M–SCN linkages are present, the cases in which linkage isomerism is observed between solid and solution indicating that the energy differences between the two forms are small.

These results are not readily rationalized in terms of either steric or electronic effects in isolation (indeed, since steric and electronic effects are interrelated, separation is to some extent impossible). It is relevant to note that Carty[16] concluded from studies on monodentate acetylenic phosphine complexes that platinum(II) exhibited a tendency to favor N bonding over analogous palladium(II) complexes, while for our *o*-phenylene series of ligands, *o*-$C_6H_4(EPh_2)(E'Ph_2)$ (E, E′ = P, As, Sb), we[5,6] have previously observed a tendency for platinum(II) to change from N,S to S,S coordination earlier than palladium(II) along the series as E, E′ changes from P, P to Sb, Sb.

Clearly the mode of thiocyanate coordination in complexes of these two metals with bidentate group 5B ligands is controlled by a very subtle interplay of steric and electronic factors and cannot at the present time be rationalized in detail.

Registry No. Pt(dpm)(SCN)$_2$, 59301-86-9; Pt(dpe)(NCS)(SCN), 59301-81-4; Pt(dpp)(NCS)(SCN), 59301-82-5; Pt(vpp)(NCS)(SCN), 59301-83-6; Pt(vpa)(NCS)(SCN), 59301-84-7; Pt(vaa)(SCN)$_2$, 59301-79-0; Pt(dae)(SCN)$_2$, 59301-78-9; Pt(pae)(NCS)(SCN), 59301-85-8; Pd(pae)(SCN)$_2$, 59331-86-1; dithiocyanatobis(benzonitrile)platinum(II), 59301-80-3.

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Contribution from the Research School of Chemistry,
Australian National University, Canberra, ACT,
Australia 2600, and the Department of Chemistry,
Queen's University, Belfast BT9 5AG, Northern Ireland

γ-Carbon-Bonded 2,4-Pentanedionato Complexes of Trivalent Iridium

M. A. Bennett* and T. R. B. Mitchell

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Despite the thermal and oxidative stability of octahedral iridium(III)–carbon σ-bonded complexes, there are no well-characterized γ-C-bonded β-diketone complexes of iridium(III) analogous to the well-known derivatives of octahedral platinum(IV)[1] and of planar platinum(II)[1] and palladium(II).[2] Gibson[3] has reported that K$_3$IrCl$_6$ reacts with an excess of potassium acetylacetonate in aqueous solution to give, among other products, a complex tentatively formulated as K$_2$Ir$_2$(acac)$_7$Cl·H$_2$O which may contain γ-C-bonded acac groups.[4] In the course of an attempt to improve on the literature synthesis of Ir(acac)$_3$, **1**,[5] we have isolated some iridium(III) complexes which appear to contain both O- and C-bonded acac groups. The preparations and spectroscopic evidence for the formulations are reported in this note.

Experimental Section

Measurements. Ir spectra were recorded on a PE457 spectrophotometer using either KBr disks or 1-mm path length solution cells with KBr windows. Mass spectra were measured by Mr. G. Jordan (Queen's University) on an MS-902 instrument at 70 eV. ^{1}H NMR spectra (Table I) were run on a Varian HA-100 spectrometer by Mr. I. Jack and ^{13}C NMR spectra (Table II) on a Bruker WH90FT instrument by Dr. L. C. Waring (Queen's University). Microanalyses (Table III) were carried out in the departmental microanalytical laboratories by Miss Brenda Stevenson and Dr. Joyce Fildes and their associates (Australian National University) and by Messrs. B. McKnight and D. McClure (Queen's University).

Preparations. Bis(2,4-pentanedionato-*O,O*)(2,4-pentanedionato-*C*^{3})pyridineiridium(III), 3. Hydrated iridium trichloride (1.05 g), 2,4-pentanedione (10 ml), and sodium bicarbonate (2 g) were heated under reflux in a nitrogen atmosphere for 40 h. The excess of diketone was removed in vacuo and the yellow residue was extracted with three 15-ml portions of dichloromethane. The extract was evaporated to ca. 5 ml and chromatographed on neutral alumina. The yellow band which eluted with benzene gave tris(2,4-pentanedionato-*O,O*)iridium(III), **1** (0.23 g, 18%),[5] identified by its ^{1}H NMR spectrum (Table I). The bright yellow solid (2.70 g) which remained after extraction with dichloromethane was heated under reflux with pyridine (40 ml) in a nitrogen atmosphere for 2 h. After filtration and evaporation to dryness, **3** was obtained as a lemon yellow solid (0.83 g, 49%) which was purified by recrystallization from dichloromethane–ether.

Bis(2,4-pentanedionato-*O,O*)(2,4-pentanedionato-*C*^{3})(*p*-toluidine)iridium(III), 4. The dichloromethane-insoluble solid **2** obtained as described above from hydrated iridium trichloride (0.29 g) was stirred with excess *p*-toluidine (5 g) at 100 °C in a nitrogen atmosphere for 2 h. After cooling of the mixture to room temperature, ether (25 ml) was added, and the precipitated solid was dissolved in dichloromethane (5 ml). Chromatography on neutral alumina and elution with chloroform gave a yellow band, which, after evaporation of solvent and recrystallization of the residue from dichloromethane–ether, gave **4** as a lemon yellow solid (0.14 g, 29%).

Bis(μ-2,4-pentanedionato-*O,O,C*^{3})-bis(2,4-pentanedionato-*O,O*)bis(2,4-pentanedionato-*C*^{3})diiridium(III), 5. Solid **2** obtained from hydrated iridium trichloride (1.00 g) was boiled for 1 h with water (120 ml) to give an orange solution. This was evaporated to dryness in vacuo and the residue was extracted with two 50-ml portions of dichloromethane. Chromatography on neutral alumina, elution with chloroform, and crystallization from chloroform–ether gave **5** as an orange solid (0.62 g, 45%).

Bis(2,4-pentanedionato-*O,O*)(2,4-pentanedionato-*C*^{3})ammineiridium(III), 6. Compound **5** (0.103 g) was stirred with aqueous ammonia (0.880) (25 ml) for 2 h, the mixture being warmed gently. The mixture was worked up as described above for **5**, and the product was recrystallized from chloroform–ether to give a lemon yellow solid (0.060 g, 57% based on **5**).

Bis(2,4-pentanedionato-*O,O*)(2,4-pentanedionato-*C*^{3})(*n*-propylamine)iridium(III), 7. Compound **5** (0.103 g) was heated under reflux with an excess of *n*-propylamine for 2 h. After removal of amine in vacuo the solid was purified as described for **5**. Compound **7** was obtained as a yellow-orange solid (0.059 g, 52% based on **5**) from dichloromethane–ether.

Results and Discussion

Tris(2,4-pentanedionato-*O,O*)iridium(III), **1**, was first prepared[5] in only 10% yield by heating freshly precipitated iridium(III) hydroxide with 2,4-pentanedione at pH 6 for 1 h. We tried to improve on this by adapting a method which has given good yields of tris(β-diketonato) complexes of ruthenium(III).[6] On heating chloroiridic acid or hydrated iridium trichloride with a large excess of neat 2,4-pentanedione and sodium bicarbonate, **1** is formed in 18% yield together with a yellow solid, **2**, which is insoluble in dichloromethane and other organic solvents. We have been unable to purify this solid or obtain reproducible analytical data for it, probably owing to the presence of sodium acetylacetonate and sodium chloride in addition to polymeric 2,4-pentanedionato complexes of iridium. However, **2** reacts with boiling pyridine to give a bright yellow, crystalline solid of empirical formula Ir(acac)$_3$py, **3**, which is soluble in chloroform and dichloromethane and is monomeric in the former solvent. The mass spectrum of **3** shows a parent ion. Compound **2** reacts with *p*-toluidine at 100 °C to give yellow Ir(acac)$_3$(*p*-CH$_3$C$_6$H$_4$NH$_2$), **4**, and with boiling water to give a yellow complex **5** of empirical formula Ir(acac)$_3$ which is dimeric in chloroform. The yields in all three preparations are 30–50% based on iridium. Compound **5** reacts with pyridine to give **3** and with ammonia or *n*-propylamine to give yellow, crystalline derivatives of formula Ir(acac)$_3$L (L = NH$_3$ (**6**) or *n*-PrNH$_2$ (**7**)). Similar adducts containing triphenylphosphine, dimethylphenylphosphine, *N*-methylaniline, or *N,N*-dimethylaniline could not be obtained.

The ir spectra of the O-bonded complexes M(acac)$_3$ (M = Rh or Ir) and of the adducts Ir(acac)$_3$L (**3**, **4**, **6**, and **7**) show

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* To whom correspondence should be addressed at Australian National University.