binuclear system and is not applicable in this form to trinuclear systems (the right formulas are given in ref 15). In ref 1 there is a statement that the antisymmetric exchange parameter $D \neq 0$ in a distorted system only. Actually the antisymmetric exchange interaction is larger for trigonal clusters (nondistorted) (in this connection see refs 14, 16, 17, and 18 dealing with the analysis of Heisenberg model and application of the theory of ESR spectra and thermodynamic properties). The expression "nondegenerate Kramers doublets"[1] is inadequate. In a system of six interacting spins (an even number of electrons) Kramers doublets cannot exist at all.

The above indicates that additional efforts are needed to achieve an adequate interpretation of the experimental data dealing with polynuclear transition-metal clusters.

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Correlation between the Trans Influence of a Ligand L and the Electronegativity of the Donor Atom in a Series of Hydridoiridium(III) Complexes *trans*-H(L)Ir(CO)(Cl)(PPh$_3$)$_2$

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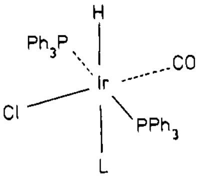
Received May 7, 1982

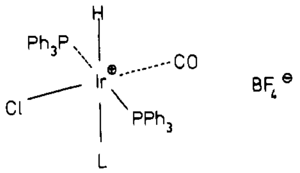
The trans influence of a ligand has been defined as the extent to which this ligand weakens the bond trans to itself.[1]

Many studies—mainly with square-planar platinum(II) complexes—have been made in order to correlate the trans influence of a ligand with physical data,[2] using different techniques such as infrared, NMR (chemical shifts and coupling constants),[3] X-ray crystallography,[4] quadrupole resonance,[5] photoelectron,[6] and Mössbauer spectroscopy.[7] The synthesis of a series of octahedral, neutral, and cationic hydridoiridium(III) complexes **1** and **2**[11] provides the possibility to study the trans influence of various anionic and neutral ligands on the hydride ligand. For hydridoiridium(III) complexes previously Chatt et al.,[8] Vaska,[9] and Wilkinson et al.[10] have observed that ν(Ir–H) and the NMR chemical shift of the hydride is dependent on the ligand trans to hydride. A comparison of δ(IrH) ^{1}H NMR chemical shifts and the wavenumbers of ν(IrH) and ν(CO) stretching vibrations (Table I) of complexes **1** and **2** leads to the following conclusions:



1

L = *Se*CN$^-$, *N*CSe$^-$, $OSO_2CF_3^-$,
$OSO_2C_4F_9^-$, FBF_3^-



2

L = PPh$_3$, CNC$_6$H$_{11}$, NCMe, OH$_2$, OCMe$_2$, THF
*N*CSe[Ir(H)(Cl)(CO)(PPh$_3$)$_2$]
*Se*CN[Ir(H)(Cl)(CO)(PPh$_3$)$_2$]

Table I. δ(IrH) ^{1}H NMR Chemical Shift[a] and ν(Ir–H) and ν(CO) Wavenumbers of Complexes 1 and 2

	δ(Ir–H) (CD_2Cl_2)	ν(Ir–H) (Nujol)	ν(CO) (Nujol)
$(Ph_3P)_2(CO)ClHIr\mathit{F}BF_3$	−26.5	2333	2061
$(Ph_3P)_2(CO)ClHIr\mathit{O}SO_2C_4F_9$	−21.86	2301	2063
$(Ph_3P)_2(CO)ClHIr\mathit{O}SO_2CF_3$	−21.77	2305	2055
$[(Ph_3P)_2(CO)ClHIr(\mathit{O}C_4H_8)]^+BF_4^-$	−22.24	2305	2042
$[(Ph_3P)_2(CO)ClHIr(\mathit{O}C_3H_6)]^+BF_4^-$	−21.39		2057
$[(Ph_3P)_2(CO)ClHIr(\mathit{O}H_2)]^+BF_4^-$	−21.13	2303	2051
$\{[(Ph_3P)_2(CO)ClHIr]_2(\mathit{N}CSe)\}^+BF_4^-$	−16.80		
$[(Ph_3P)_2(CO)ClHIr(\mathit{N}CCH_3)]^+BF_4^-$	−16.44	2218	2069
$(Ph_3P)_2(CO)ClHIr(\mathit{N}CSe)$	−16.1		
$(Ph_3P)_2(CO)ClHIr\mathit{Cl}$		2240	2027
$[(Ph_3P)_2(CO)ClHIr(\mathit{C}NC_6H_{11})]^+BF_4^-$ [b]	−11.12		
$\{[(Ph_3P)_2(CO)ClHIr]_2(\mathit{Se}CN)\}^+BF_4^-$	−12.11		
$(Ph_3P)_2(CO)ClHIr(\mathit{Se}CN)$	−11.4	2180	2048
$[(Ph_3P)_2(CO)ClHIr(\mathit{P}Ph_3)]^+O_3SCF_3^-$	−9.37	2163	2039

[a] Standard $CHDCl_2$ = 5.33 ppm. [b] NMR-tube preparation.

(1) The ^{1}H NMR chemical shift of the hydride ligand depends on the donor atom trans to the hydride. All iridium(III) complexes with O-coordinated trans ligands absorb at −21.6 ± 0.6 ppm; those with N-coordinated trans ligands at −16.5 ± 0.5 ppm (Table I).

(2) The ^{1}H chemical shift of the hydride ligand is found to be independent of the charge of the complex. The neutral complexes **1** with anionic ligands trans to the hydride absorb in the same region as the cationic complexes **2** with neutral

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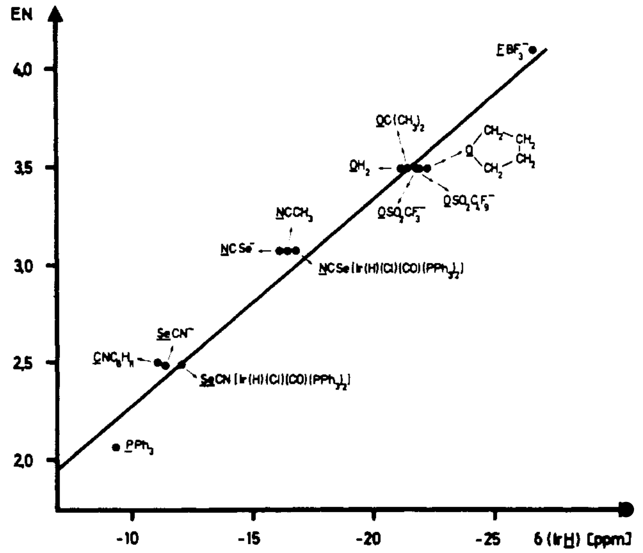

Figure 1. Plot of electronegativity (Allred–Rochow) of the trans donor atom vs. δ(IrH) for complexes **1** and **2**.

ligands L, provided the trans donor atoms are identical.

(3) A direct correlation exists between δ(IrH) and ν(IrH) (Figure 2). This was also found for a large series of hydridoplatinum(II) complexes.[2c,3d]

(4) A direct correlation also is found between the IrH chemical shift or the ν(IrH) wavenumber, respectively, and the electronegativity of the trans donor atom (Figure 1). Vaska[9] first pointed out that for analogous halide Ir(III) complexes ν(IrH) varies linearly with the electronegativity of the trans halide ligand.

(5) The change of spectral data for complexes with the same trans donor atom but in different ligands is small (Figures 1 and 2). A high-field shift of δ(IrH) is observed in the series $O_3SCF_3^- < O_3SC_4F_9^-$ for **1** and H_2O < acetone < THF for **2**, i.e. with decreasing donor strength of the trans ligand L.

(6) No direct correlation is found between δ(IrH) or ν(IrH), respectively, and the stretching frequency of the CO group cis to the hydride ligand (Figure 3).

The order of trans influence ($PPh_3 > CNC_6H_{11} >$ NCMe > acetone) found for **1** and **2** is in accordance with that for planar platinum(II) complexes.[2,3]

The change of ν(IrH) and δ(IrH) for **1** and **2** is certainly mainly due to the change of σ-donor strength of the trans ligands L. The spectral data of the ethylene complex *trans*-$[(H)(C_2H_4)Ir(CO)(Cl)(PPh_3)_2]^+$[11d] with the π donor C_2H_4 do not fit into this series of ligands.

In a theoretical study the large chemical shifts of the hydride ligand have been mainly attributed to paramagnetic shielding of the proton by the metal d electrons and the change of chemical shifts to variation of the metal–hydride distance caused by the trans ligand L.[12] Obviously, with decreasing σ-donor strength of the trans ligand L (higher electronegativity of the trans donor atom), a shortening of the Ir–H distance (higher ν(IrH) wavenumber and high-field shift of δ(IrH)) is occurring.

These results can be qualitatively explained both by the "polarization theory of the trans effect"[13] and on the basis of MO theory.[14] These findings also are good examples for Gutmann's "donor–acceptor approach".[15]

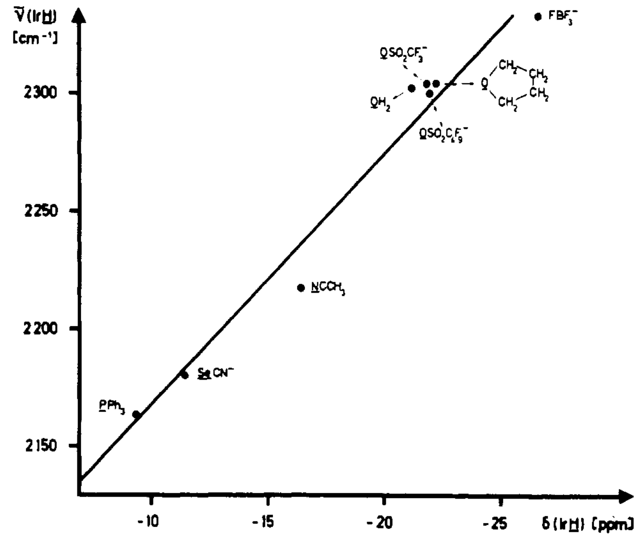

Figure 2. Plot of ν(Ir–H) vs. δ(IrH) for complexes **1** and **2**.

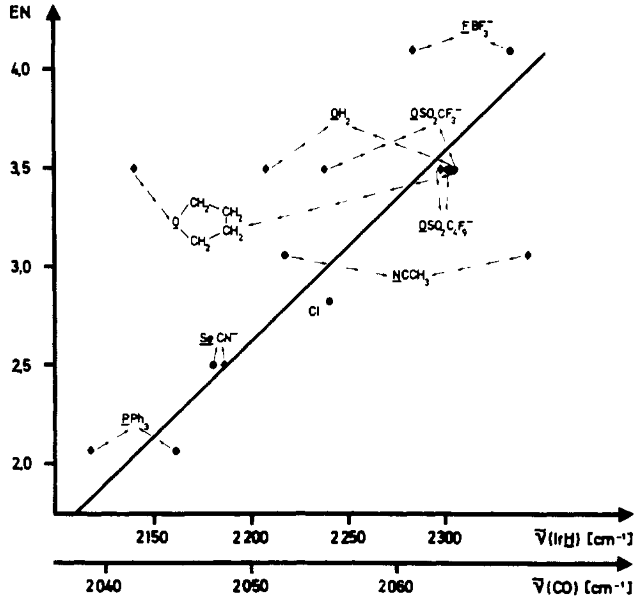

Figure 3. Plot of electronegativity of the trans donor atom vs. ν(Ir–H) (●) or ν(CO) (♦) for complexes **1** and **2**.

The observed correlation between the spectral data of the hydride ligand and the trans ligand also is useful for the structural assignment of octahedral hydridoiridium(III) complexes. Cis complexes $H(L)Ir(CO)(Cl)(PPh_3)_2$ (H and L cis) show substantial deviation from these simple, nearly linear correlations.[11c]

Acknowledgment. Support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. **1** (L = FBF_3), 75149-80-3; **1** (L = $OSO_2C_4F_9$), 79292-36-7; **1** (L = OSO_2CF_3), 78350-77-3; **1** (L = NCSe), 78571-29-6; **1** (L = Cl), 26545-07-3; **1** (L = SeCN), 78333-09-2; **2** (L = THF), 79292-49-2; **2** (L = $OCMe_2$), 79292-47-0; **2** (L = OH_2), 79292-45-8; **2** (L = $NCCH_3$), 79292-43-6; **2** (L = CNC_6H_{11}), 84500-05-0; $\{[(Ph_3P)_2(CO)ClHIr]_2(NCSe)\}^+BF_4^-$, 84500-03-8; $\{[(Ph_3P)_2(CO)ClHIr]_2(SeCN)\}^+BF_4^-$, 84500-07-2; $[(Ph_3P)_3(CO)ClHIr]^+O_3SCF_3^-$, 82474-51-9.

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