

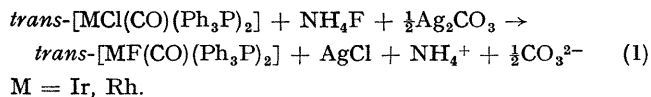
A Simple Synthetic Route to d^8 Complexes of Rhodium and Iridium. An Electronegativity Scale for Anionic Ligands

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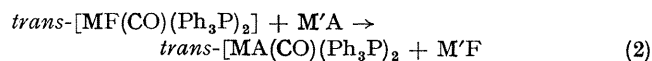
Summary Molecular fluoro-complexes *trans*-[MF(CO)(Ph₃P)₂] (M = Ir, Rh), undergo rapid substitution reactions to yield a variety of new derivatives, *trans*-[MA(CO)(Ph₃P)₂] (A = univalent anionic ligand); a relation between the ν_{CO} and "total electronegativity" of A in these compounds is suggested.

THE discovery of molecular fluoro-complexes of univalent iridium and rhodium by reaction (1) has provided a convenient—and in many cases unique—preparative route (2)



to a variety of compounds of these metals. The rapid

substitutions (2) owe to the lability of the fluoro-ligand in [MF(CO)(Ph₃P)₂] when dissolved in polar solvents (see eq. 3).

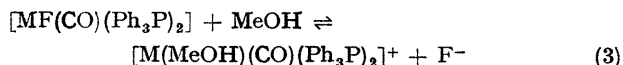


A = univalent anionic ligand (see Table); M' = Li, Na or K.

The fluoro-complexes have been synthesized by the following procedure: powdered [MCl(CO)(Ph₃P)₂] is treated with a saturated solution of NH₄F in methanol and the resulting suspension is boiled until most of the reactant complex dissolves. Silver carbonate (Ag:M = 1) is then added and boiling is continued for 1—3 min. during which time Ag₂CO₃ dissolves and AgCl precipitates. The latter is separated by filtration and the hot filtrate is mixed with an aqueous solution of NH₄F (0.1 M) whereupon yellow

crystals of the product form in 80–90% yield. Correct elemental analyses have been obtained for both complexes; $\nu_{\text{Ir-F}}$, 451 cm^{-1} .

The crystals of $[\text{RhF}(\text{CO})(\text{Ph}_3\text{P})_2]$ are air-stable, but those of the iridium analogue decompose slowly and must be stored under N_2 . The complexes are non-conductors in acetone and nitrobenzene. In methanol, however, they show some conductance [$\Lambda_{\text{M}} = 22$ (Ir), 35 (Rh)]; for 1:1 electrolytes the value is *ca.* 100 ohm^{-1} which points to a solvolytic equilibrium (3). The latter appears to be responsible for the ready formation of the derivatives listed



in the Table. In a typical experiment, the reactants (eq. 2, $\text{M}:\text{M}' = 1:20$) are mixed in methanol, the resulting suspension is heated to boiling (5 min.) and then poured into an equal volume of water: the product precipitates in yields from 40 to 100%, depending on the complex (Ir, Rh) and the anion (A) employed.

While the halogeno-complexes, $\text{A} = \text{Cl}, \text{Br}, \text{I}$ (given for comparison in the Table) are commonplace in current chemical literature, and the bromo-, iodo- and also some pseudohalogeno-derivatives (*e.g.*, $\text{A} = \text{N}_3, \text{NCS}$) can be obtained from the chloro-analogue by a simple substitution (*cf.* eq. 2), the latter route does not seem feasible for the majority of compounds listed in the Table.² For example, treatment of $[\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2]$ with NaNO_2 or NaNO_3 gives complex mixtures which include irreversible oxidation products and nitrosyl complexes.³

An examination of the carbonyl stretching frequencies (ν_{CO}) in *trans*- $[\text{MA}(\text{CO})(\text{Ph}_3\text{P})_2]$ (Table) suggests a correlation between the ν_{CO} and a "total electronegativity," $x_{\text{A}(\text{T})}$, or acceptor strength of the anionic ligand A *trans* to CO, defined in eq. (4), where x_{A} is a "classical" or " σ " electronegativity⁴ and $x_{\text{A}(\pi)}$ a " π -electronegativity" or " π -acidity" of A. The suggestion (4) is based on the assumptions (a) that for F, $x_{\text{A}(\pi)} = 0$ (*i.e.*, $x_{\text{A}(\text{T})} = x_{\text{F}}$) and (b) that the magnitude of $\Delta\nu_{\text{CO}}$ is a direct reflection of the

$$x_{\text{A}(\text{T})} = x_{\text{F}}(\Delta\nu_{\text{CO}^2})_{\text{F}}/(\Delta\nu_{\text{CO}^2})_{\text{A}} = x_{\text{A}} + x_{\text{A}(\pi)} \quad (4)$$

$$\Delta\nu_{\text{CO}^2} = [\nu_{\text{CO}}(\text{gas})]^2 - [\nu_{\text{CO}}(\text{complex in } \text{CHCl}_3)]^2$$

total acceptor strength of A in *this particular series* of isostructural and formally isoelectronic complexes. That is, as all electronegativity concepts, the present one can yield only relative data.

It is to be noted that (i) the sequence of the ν_{CO} or the $x_{\text{A}(\text{T})}$ values is the same for the iridium and rhodium series of complexes and, more importantly, (ii) the orders of π -acidity, $x_{\text{A}(\pi)}$, computed by eq. (4), are nearly identical for the two metals. (iii) For *trans*- $[\text{RhA}(\text{CO})(\text{Ph}_3\text{P})_2]$, $x_{\text{A}(\pi)}$ decreases as follows: $\text{I} > \text{SePh} > \text{Br} > \text{SPh} > \text{CN} > \text{Cl} > \text{NO}_2 > \text{NCS} \sim \text{N}_3 > \text{ONO}_2 > \text{NCO} > \text{OCO}(\text{Me}) > \text{OCO}(\text{Ph}) > \text{OPh} > \text{OH} = \text{F}$ [the Ir series gives the same sequence except that the positions of Cl and NO_2 are inverted;

$\text{N}(\text{CN})_2, \text{NCSe}, \text{OCIO}_3$, and $\text{OCO}(\text{H})$ are omitted because of the uncertainties involved, see footnotes e and f to the Table]. (iv) Perhaps the most significant support for the

TABLE

Carbonyl stretching frequency (ν_{CO}) in *trans*- $[\text{MA}(\text{CO})(\text{Ph}_3\text{P})_2]^{\text{a}}$ ($\text{M} = \text{Ir}, \text{Rh}$), and electronegativity (x_{A}) and "total electronegativity" [$x_{\text{A}(\text{T})}$, see eq. (4) and text] of the anionic ligand A

	A ^b	x_{A}^{c}	$x_{\text{A}(\text{T})}^{\text{d}}$		$\nu_{\text{CO}}, \text{cm}^{-1}$ in CHCl_3	
			Ir	Rh	Ir	Rh
CN	..	3.38	4.79	4.90	1990	2003
NCSe	..	(3.7) ^e	4.76	4.87	1987	2002
NO_2	..	3.45	4.76	4.67	1987	1996
$\text{N}(\text{CN})_2$..	(3.2) ^e	4.64	4.65	1983	1995
OCIO_3	..	3.70	4.62	4.55	1982 ^f	1992 ^f
NCS	..	3.64	4.46	4.50	1976	1990
ONO_2	..	3.65	4.33	4.36	1971	1985
SePh	..	2.32	—	4.29	—	1982
NCO	..	3.60	4.26	4.28	1968	1982
I	..	2.22	4.24	4.26	1967	1981
Br	..	2.58	4.21	4.23	1966	1980
Cl	..	2.94	4.19	4.23	1965	1980
N_3	..	3.38	4.19	4.23	1965	1980
SPh	..	2.58	—	4.22	—	1980
$\text{OCO}(\text{H})$..	(3.6) ^e	—	4.21	—	1979
$\text{OCO}(\text{Ph})$..	3.67	—	4.06	—	1973
$\text{OCO}(\text{Me})$..	3.60	—	4.04	—	1972
F	..	4.02	4.02	4.02	1957	1971
OPh	..	3.74	—	4.00	—	1970
OH	..	3.89	3.89	3.89	1949	1961

^a The compounds have been characterized by their i.r. and electronic spectra, and most of them (24 of the 34 listed) by elemental analyses. The vibrational frequencies of the polyatomic anionic ligands also give unambiguous evidence for the complexes as formulated. Conductance data of selected compounds in methanol, acetone, or nitrobenzene show that they are non-electrolytes in these solvents; the nitrate- and perchlorate-complexes, however, undergo partial and complete ionization, respectively (*cf.* eq. 3).

^b The metal-bonded atom is given first.

^c Calculated by Willmhurst equation, ref. 4.

^d See equation (4).

^e Estimated.

^f Measured in benzene.

validity of eq. (4) emerges from the fact that it gives $x_{\text{OH}(\pi)} = 0$ for both of the hydroxo-complexes, $[(\text{Ir}, \text{Rh})\text{OH}(\text{CO})(\text{Ph}_3\text{P})_2]$, in accordance with the common notion that this ligand is unable to act as a π -acceptor; note also the expected low π -acidity of the phenoxo group ($x_{\text{OPh}(\pi)} = 0.26$). (v) Finally, the order of the ν_{CO} values in the halogeno-complexes, $\text{A}: \text{I} > \text{Br} > \text{Cl} > \text{F}$ (although the differences are small, they are definite for $\text{M} = \text{Ir}$), not explicable by the conventional electronegativity concept, x_{A} , finds a natural interpretation in terms of the currently accepted theory of σ - π dualism.

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¹ These unusual compounds are more fully described elsewhere, J. Peone, jun., and L. Vaska, submitted for publication.

² $[\text{Rh}(\text{OH})(\text{CO})(\text{Ph}_3\text{P})_2]$ has been synthesized previously by a different method, G. Gregorio, G. Pregaglia, and R. Ugo, *Inorg. Chim. Acta*, 1969, 3, 89.

³ P. Carty, A. Walker, M. Mathew, and G. J. Palenik, *Chem. Comm.*, 1969, 1374.

⁴ J. K. Willmhurst, *J. Chem. Phys.*, 1958, 28, 733.