Structural Aspect of CO Bonding in Pentacoordinate Ni(II) Complexes $NiX_2(CO)(PMe_3)_2$

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Received December 22, 1983

Activation of CO by transition metal complexes is a very active research field and is related to organometallic synthesis and homogeneous catalysis. In order to understand the reaction mechanism and the nature of the intermediates, it is important to have simple complexes where simple chemical changes can be made and the effects of these changes on the chemical bond can be studied.

We have already characterized chemically and structurally $NiI_2(CO)(PMe_3)_2$, which belongs to the rare Ni(II)–CO complexes [1]. This compound was kinetically unstable, and presented the shortest Ni–CO bond length ever reported. A straightforward chemical change was to replace the iodine atom by a chlorine atom and determine its influence on the Ni–CO bond. We would expect that in π complexes the bonding changes with chemical substitution, if the electron density at the central atom changes. Such a change can be ascribed to a greater electron density at the metal when X = I compared to X = Cl. The infrared spectrum shows a slight energy shift to lower frequencies from 2015 cm^{-1} (I) to 2005 cm^{-1} (Cl), indicating more back donation in the chloro than in the iodo complex. The same trend is observed for the $^{31}P\{^1H\}$ NMR chemical shift, where a greater shift to lower field is observed for the chloro complex (83.6 ppm) than for the iodo (68.6 ppm). On the other hand, the chloro complex readily loses CO in the solid state and is less stable than the iodo complex, which can be handled in air for a few minutes. If an inert gas is bubbled through the solution, both complexes lose CO and the parent $NiX_2(PMe_3)_2$ compound can be recrystallized.

We thought thus it was of interest to see if these differences could result in detectable structural changes.

$NiCl_2(CO)(PMe_3)_2$ was directly obtained as suitable single crystals (dark brown spheroids) from an acetone solution at –25 °C. The resolution of the structure [2] shows that the two complexes $NiX_2(CO)(PMe_3)_2$ (X = Cl and X = I) are isomorphous [3].

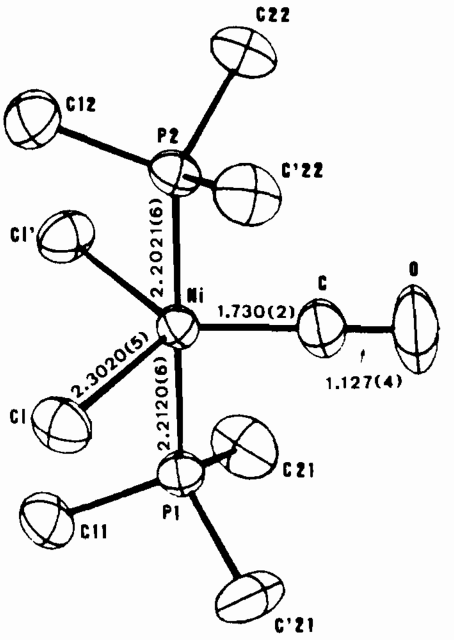

Fig. 1. ORTEP drawing of $NiCl_2(CO)(PMe_3)_2$.

The inner coordination sphere around the nickel is shown in Fig. 1. The distances and angles are reported on Table I, and are directly compared to the values of $NiI_2(CO)(PMe_3)_2$.

Both complexes are trigonal bipyramidal with CO and the two halides located in the equatorial plane as expected [4]. The plane P1,P2,Ni,C,C is a mirror plane of the molecule.

The Ni–CO distance is similar in both complexes (1.730(2) Å, X = Cl; 1.728(23) Å, X = I) and the difference of the C–O distances is not significant. Considering 0.99 Å (Cl) and 1.33 Å (I) as the normal covalent radii of the halides, one may evaluate the covalent radius of Ni(II) in five coordinate trigonal bipyramidal complexes: 1.29(2) Å, and thus estimate a theoretical Ni–C distance considering the single bond covalent radius of C to be 0.77 Å. Under these conditions, the length of the single σ Ni–CO bond would be 2.06 Å, a value in agreement with the Ni–C distance of 2.034(7) Å found in $\{Ni(CH_3)(PMe_3)_4\}BPh_4$ [5] and 1.999(6) Å in $Co(C_6H_5)(C_2H_4)(PMe_3)_3$ [6], where CH_3 and C_6H_5 are located in the axial and equatorial site respectively of the TBP. Thus, the short Ni–C distance of 1.730(2) Å indicates the presence of extensive π back bonding from Ni $dx^2 - y^2$, dxy orbitals to $\pi^*(CO)$ and thus of a multiple Ni=C=O bond.

The Ni–Cl distance of 2.3020(5) Å is in the range where are found the metal–chlorine distances. The difference in bond length between Ni–Cl and Ni–I is equivalent to the difference between single bond

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0020-1693/84/$3.00

TABLE I. Intramolecular Main Bonds and nonbonded Distances (Å) and Angles (°) in $NiCl_2(CO)(PMe_3)_2$. The corresponding values for $NiI_2(CO)(PMe_3)_2$ are in italics.

Distances around Ni:						
Ni–Cl	2.3020(5)		*Ni–I*	*2.6048(13)*		
Ni–P(1)	2.2120(6)			*2.225(5)*		
Ni–P(2)	2.2021(6)			*2.215(5)*		
Ni–C	1.730(2)			*1.728(23)*		
C–O	1.127(4)			*1.137(20)*		
Angles around Ni:						
Cl–Ni–Cl	107.30(2)	*I–Ni–I*	*112.23(7)*	P(1)–Ni–P(2)	179.86(4)	*179.7(3)*
Cl–Ni–P(1)	90.63(2)	*I–Ni–P(1)*	*90.15(9)*	P(1)–Ni–C	90.55(8)	*90.0(6)*
Cl–Ni–P(2)	89.45(2)	*I–Ni–P(2)*	*89.66(8)*	P(2)–Ni–C	89.32(8)	*90.4(6)*
Cl–Ni–C	126.33(1)	*I–Ni–C*	*123.88(4)*	Ni–C–O	179.8(2)	*179.2(19)*
Distances and Angles around P atoms:						
P(1)–C(11)	1.808(3)	*1.800(17)*	P(2)–C(12)		1.795(3)	*1.803(18)*
P(1)–C(21)	1.806(2)	*1.834(10)*	P(2)–C(22)		1.805(2)	*1.800(11)*
Ni–P(1)–C(11)	113.97(9)	*116.7(5)*	Ni–P(2)–C(12)		113.41(9)	*117.4(5)*
Ni–P(1)–C(21)	113.23(7)	*113.5(4)*	Ni–P(2)–C(22)		113.86(7)	*113.4(4)*
C(11)–P(1)–C(21)	104.78(8)	*104.1(5)*	C(12)–P(2)–C(22)		103.95(9)	*103.5(5)*
C(21)–P(1)–C(21)	106.01(11)	*103.6(7)*	C(22)–P(2)–C(22)		106.82(13)	*104.3(8)*
Ligand–Ligand Distances[a]:						
Cl–Cl	3.7081(8)	*I–I*	*4.3248(15)*	C–P(1)	2.821(3)	*2.816(22)*
Cl–C	3.607(2)	*I–C*	*3.845(19)*	C–P(2)	2.784(3)	*2.818(19)*
Cl–P(1)	3.2098(7)	*I–P(1)*	*3.430(3)*			
Cl–P(2)	3.1704(6)	*I–P(2)*	*3.409(4)*			

[a] Van der Waals distances [9]: X–X = 3.60 Å (Cl), 4.30 Å (I); P–X = 3.70 Å (Cl), 4.05 Å (I); C–P = 3.70 Å (rC = 1.80 Å); C–X = 3.60 Å (Cl), 3.95 Å (I).

covalent radii of Cl and I (about 0.33 Å). Moreover, substitution of I by Cl, which would be expected to change the electron density at the central atom, shows no bonding change in the Ni–CO nor in the Ni–P groups. This phenomenon has already been observed in metal carbonyl compounds, and is related to the presence of synergetic $\sigma + \pi$ bonding [7]. Following the nature of the metal and ancillary ligands and the stereochemistry of the complex, it has been suggested that either there is no halogen influence on CO force constant or on the M–CO bond distance, or a lower energy fit following the decrease of electronegativity, or an opposite *cis-trans* influence of X [8].

The other significant difference in the structures of the two complexes is the values of the angles in the equatorial plane: Cl–Ni–Cl (107.30(2)°) is significantly smaller than I–Ni–I (112.23(7)°), and consequently the Cl–Ni–C (126.33(1)°) is larger than I–Ni–C (123.88(4)°). This can be related to the different steric demand of the two halides and to the packing in the crystal. However, calculation of the ligand–ligand non-bonding distances and comparison with the sum of the van der Waals radii of the different atoms indicate that the non-bonding contacts are similar in the two complexes and that the C–P distance is very short (Table I). Thus the difference between Cl–Ni–Cl and I–Ni–I may be electronic in origin.

In conclusion, the X-ray structure shows no influence of the electronegativity of the halide on the Ni–CO distance in $NiX_2(CO)(PMe_3)_2$ (X = Cl, I). In both complexes, this distance is very short and thus is indicative of an extensive π back bonding: Ni=C=O. This result has however to be considered along with the chemical properties of the complexes which show that the more electropositive iodine ligand gives rise to a kinetically more stable complex.

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2 *Crystal data*: $NiCl_2OP_2C_7H_{18}$, orthorhombic, space group *Pnma*, a = 9.788(1), b = 10.340(1), c = 13.665(3) Å, V = 1383 Å^3, $Z = 4$, d_c = 1.487 g cm^{-3}, μ(Mo-K$\bar{\alpha}$) = 20.1 cm^{-1}, R = 0.020, Rw = 0.024 for 1599 observed data having $I \geqslant 3\sigma(I)$ and $1.5° < \theta < 28°$. 5034 intensities were collected in the $\theta - 2\theta$ scan mode using graphite monochromatized Mo-K$\bar{\alpha}$ radiation, λ = 0.71069 Å (Enraf-Nonius CAD 4 diffractometer) and averaged to give 2341 independent reflections. The structure was solved by conventional heavy atom methods and refined by full-matrix least-squares, treating non-hydrogen atoms anisotropically.

3 The decreased size of Cl compared to I is apparent on the unit cell dimensions. $NiI_2OP_2C_7H_{18}$: a = 10.495(1), b = 10.744(1), c = 14.047(5) Å and V = 1584 Å^3.

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