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Registry No. *cis*-$[Cr(CO)_2(DPM)_2]^+$, 66700-92-3; *cis*-$[Mo(CO)_2(DPM)_2]^+$, 66700-91-2; *cis*-$[W(CO)_2(DPM)_2]^+$, 66700-90-1; *cis*-$[Cr(CO)_2(DPE)_2]^+$, 37753-97-2; *cis*-$[Mo(CO)_2(DPE)_2]^+$, 37684-59-6; *cis*-$[W(CO)_2(DPE)_2]^+$, 37684-60-9; *trans*-$Cr(CO)_2(DPM)_2$, 66700-95-6; *trans*-$Mo(CO)_2(DPM)_2$, 26743-82-8; *trans*-$W(CO)_2(DPM)_2$, 66700-94-5; *trans*-$Cr(CO)_2(DPE)_2$, 31320-75-9; *trans*-$Mo(CO)_2(DPE)_2$, 40219-77-0; *trans*-$W(CO)_2(DPF)_2$, 51202-31-4; *trans*-$Mo(CO)_2(DPP)_2$, 66700-93-4; $Mo(CO)_2(DPP)_2$, 66633-00-9; $Mo(CO)_6$, 13939-06-5.

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Association Reactions and Equilibrium Constants in Tetracoordinate Iridium(I) Complexes

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Reversible association reactions of a neutral molecule to a potential catalyst d^8 tetracoordinate complex can be considered as a model of one of the steps involved in the catalytic process. Here are reported the reactions of triphenylphosphine addition to a number of isostructural and isoelectronic complexes of the type $Ir(NO)(cat)(PPh_3)$ (cat = catecholato) having different catecholato ring substituents to give the corresponding series of pentacoordinate $Ir(NO)(cat)(PPh_3)_2$ complexes. The equilibrium constants relative to the pentacoordinate species formation have been determined by IR measurements of the tetracoordinate nitrosyl band intensity at different equilibrium positions. The equilibrium constant values are discussed in terms of electron density of the central metal and electron-releasing or -withdrawing power of the catecholato ring substituents. The plot of $\log K_{eq}$ vs. $\nu(NO)$ for the tetracoordinate species gives a good linear dependence confirming that $\nu(NO)$ is a good test of the relative electronic situation on the metal in such classes of complexes. Moreover, it is pointed out that the plot of $\log K_{eq}$ vs. $pK_a{}^I$ of the free, differently substituted catechols provides a useful tool to predict the electron density on the central metal and, consequently, its ability to associate neutral molecules of catalytic interest such as unsaturated hydrocarbons.

Introduction

Transition-metal complexes homogeneously catalyze numerous organic reactions. Catalysis is attributed to the ability of the metal complexes in solution to reversibly coordinate reacting molecules, orienting them in adjacent sites and thereby creating a low-energy pathway for bond making and bond breaking. In addition, the catalytic circles of many processes must be visualized as varying sequences of elementary organometallic reactions. These reaction steps include availability of a coordinatively unsaturated metal center (four-coordinate d^8 complexes figure prominently), coordination of an unsaturated molecule (e.g., an alkene) to the metal center, oxidative addition of a saturated molecule (e.g., hydrogen), combination of the ligands within the coordination sphere, and dissociation of the product. Several plausible mechanisms, specially in the case of homogeneous hydrogenation, have resulted from extensive studies. Two main pathways are generally operating in this case: (i) a hydride route in which the primary step is the formation of a hydrido species and (ii) an unsaturated route in which the primary step is the coordination of the unsaturated molecule. Generally it is assumed that both pathways are simultaneously operating in every catalytic cycle. The extensively studied chemistry of the iridium(I) Vaska's compound offers several good and appropriate examples of both pathway situations. In fact, it has been demonstrated that the stability trend of the iridium(III) dihydride derivative of Vaska's complex, $H_2IrX(CO)(PPh_3)_2$, reflects the electronegativity trend of the changed ligand X (more electronegative, less stable) and the basicity scale of the phosphine group[2] (more basic, more stable). When we turn to consider the unsaturate route, the synergic character of the metal–alkene bond must be taken into account. The relative importance of the σ and π components of the metal–alkene bond depends either on the metal electron density or on the substituents attached to the olefinic double bond,[3] both influencing the stability of the organometallic complex. Significant results on the role played by the metal have been obtained by Strohmaier, who measured the associative constants of reactions between dimethyl maleate and various $IrX(CO)(PPh_3)_2$ complexes, changing with X the electron density on the metal.[4] The found trend indicates increasing stability of the olefin complexes with decreasing electron density of the iridium atom. The olefinic ligands are characterized by the presence of sufficiently energetic low-lying unoccupied molecular orbitals. In addition to unsaturated hydrocarbons, ligands such as CO, NO, and CN^- together with tertiary phosphines, arsines, and stibines constitute the most important examples of this group of π-acid ligands. The above

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summarized considerations about the organometallic reactions involved in a catalytic hydrogenation cycle and the stability of the catalyst–substrate intermediate complex lead to the conclusion that a reversible association reaction of a neutral molecule to a potential catalyst d^8 tetracoordinate complex can be considered as a model of one of the steps involved in the overall catalytic process. In the specific case reported here the tetracoordinate d^8 iridium–nitrosyl–catecholato complexes, Ir(NO)(cat)(PPh_3), which have been positively tested as hydrogenation catalysts,[5] add reversibly triphenylphosphine to give the pentacoordinate species. From a model point of view the pentacoordinate species can be considered as an intermediate complex formed during one step of the catalytic cycle between the tetracoordinate catalyst and a substrate molecule. On the other hand, the catalyst's activity and selectivity depend on a number of properties such as electron transferability, bond stability, coordination sites available, and electron configuration, which change from species to species, so that the comparison of catalytic activity can be made only between complexes of homogeneous series. The system which we have studied offers good chances in this direction because the equilibrium constants determined for eq 1 give an indirect quantitative dependence of the electron density on the metal upon the electronic behavior of the catecholato substituents.

Experimental Section

Synthesis of the Complexes. Apparatus. All of the reactions have been carried out in an atmosphere of nitrogen which has been purified by passing through a column of R3-11 BASF deoxygenating catalyst and then dried over molecular sieves. The subsequent workups of the reaction mixtures have been carried out in air. Infrared spectra have been recorded with a Perkin-Elmer 180 (4000–180 cm^{-1}) instrument. Elemental analyses were determined by the microanalysis laboratory of the Institute of Farmacia, Universitã di Pisa, Pisa, Italy. All solvents were deoxygenated prior to use and the transfers were carried out with flexible-needle or syringe techniques. The methyl ester of 3,4-dihydroxybenzoic acid was prepared from 3,4-dihydroxybenzoic acid; 3,4-hydroxybenzyl alcohol was prepared from 3,4-dihydroxybenzaldehyde. Chloranil was Fluka A.G. purum grade product and was used throughout. All other chemicals were Aldrich reagent grade products and were recrystallized before use. The complex $Ir(NO)(CH_3CN)_2L_2^{2+}$ was prepared as previously reported.[6]

Preparation of Ir(NO)(1,2-$O_2C_6H_3$-4-CH_3)(PPh_3)$_2$, 8b. To a suspension of 0.5 mmol of $Ir(NO)(CH_3CN)_2(PPh_3)_2^{2+}$ in 3 mL of methanol, 7 mL of a methanolic solution containing 0.6 mmol of 4-methyl-1,2-hydroxybenzene and the stoichiometric amount of sodium hydroxide was added. The mixture was stirred for 2 h at room temperature and then taken to dryness under reduced pressure. After addition of 10 mL of diethyl ether, the solution was clarified by filtration, and 5 mL of hexane containing 0.3 mmol of triphenylphosphine was added. The solution, after evaporation to a small volume at reduced pressure, gave a brown precipitate which was filtered, washed with hexane, and dried under vacuum (yield 60%). Anal. Calcd for $C_{43}H_{36}IrNO_3P_2$: C, 59.44; H, 4.17; N, 1.61. Found: C, 58.51; H, 4.02; N, 1.53.

General Procedure for Preparation of Pentacoordinate Complexes. As an improvement of the method previously reported,[7] all pentacoordinate complexes were synthesized reducing the solvent volume used. In a typical preparation, 5 mL of a methanolic solution containing 0.25 mmol of the appropriate catechol with the stoichiometric amount of sodium hydroxide was added to a suspension of 0.2 mmol of $Ir(NO)(CH_3CN)_2(PPh_3)_2^{2+}$ in 2 mL of methanol. The mixture was stirred for 5 h at room temperature. The light brown precipitate obtained was filtered and recrystallized from benzene–petroleum ether containing a small amount of triphenylphosphine to give yellow to brown microcrystals. In addition to previously characterized complexes,[7] the following new compounds were synthesized by this procedure.

Ir(NO)(1,2-$O_2C_6Cl_4$)(PPh_3)$_2$, 1b, quantitative yield. Anal. Calcd for $C_{42}H_{30}Cl_4IrNO_3P_2$: C, 50.82; H, 3.02; N, 1.41. Found: C, 50.65; H, 2.98; N, 1.39.

Ir(NO)(1,2-$O_2C_6H_3$-4-CH_2OH)(PPh_3)$_2$, 6b, 85% yield. Anal. Calcd for $C_{43}H_{36}IrNO_4P_2$: C, 58.36; H, 4.10; N, 1.50. Found: C, 57.98; H, 4.13; N, 1.49.

Ir(NO)(1,2-$O_2C_6H_4$)(PPh_3)$_2$, 7b, 70% yield. Anal. Calcd for $C_{42}H_{34}IrNO_3P_2$: C, 60.34; H, 4.20; N, 1.67. Found: C, 60.12; H, 4.13; N, 1.70.

Preparation of Ir(NO)(1,2-$O_2C_6H_3$-4-CH_3)(PPh_3), 8a. As an improvement of the preparation previously described, 7 mL of a methanolic solution containing 0.6 mmol of 4-methyl-1,2-dihydroxybenzene with the stoichiometric amount of sodium hydroxide was added to a suspension of 0.5 mmol of $Ir(NO)(CH_3CN)_2(P(C_6H_5)_3)_2^{2+}$ in 3 mL of methanol. The mixture was stirred for 2 h at room temperature and then taken to dryness under reduced pressure. After addition of 10 mL of diethyl ether, the suspension was passed down a silica gel column eluting with petroleum ether just to complete separation of free triphenylphosphine (TLC). The subsequent elution to remove the complex was carried out with diethyl ether. The solution so obtained was added to 10 mL of hexane and concentrated under reduced pressure. The brown microcrystalline precipitate formed was filtered, washed with hexane, and dried under vacuum (yield 55%). Anal. Calcd for $C_{25}H_{21}IrNO_3P$: C, 49.50; H, 3.46; N, 2.31. Found: C, 49.20; H, 3.38; N, 2.29.

General Procedure for Preparation of Tetracoordinate Complexes. The other tetracoordinate complexes were prepared starting from the corresponding pentacoordinate forms. In a typical preparation, the stoichiometric amount of chloranil was added to 0.5 mmol of the pentacoordinate complex dissolved in 10 mL of benzene. The solution was gently refluxed for 15 min in the air and then concentrated to small volume at reduced pressure. The residual solution was passed down a small silica gel column in petroleum ether and eluted first with benzene. In the yellow benzene fraction, triphenylphosphine oxide, 2,3,5,6-tetrachlorohydroquinone, triphenylphosphine, and chloranil were present. Then a second elution was made with diethyl ether to remove the complex stack on the silica gel. The solution so obtained was added to 10 mL of hexane and was concentrated under reduced pressure. The brown microcrystalline precipitate formed was filtered, washed with hexane, and dried under vacuum and was identified by IR spectra and elemental analysis.

Ir(NO)(1,2-$O_2C_6Cl_4$)(PPh_3), 1a: quantitative yield. Anal. Calcd for $C_{24}H_{15}Cl_4IrNO_3P$: C, 39.45; H, 2.06; N, 1.91. Found: C, 39.42; H, 2.09; N, 1.93.

Ir(NO)(1,2-$O_2C_6Br_4$)(PPh_3), 2a: 95% yield. Anal. Calcd for $C_{24}H_{15}Br_4IrNO_3P$: C, 31.74; H, 1.66; N, 1.54. Found: C, 32.06; H, 1.70; N, 1.53.

Ir(NO)(1,2-$O_2C_6H_3$-4-NO_2)(PPh_3), 3a: 92% yield. Anal. Calcd for $C_{24}H_{18}IrN_2O_5P$: C, 45.21; H, 2.84; N, 4.39. Found: C, 44.73; H, 2.79; N, 4.43.

Ir(NO)(1,2-$O_2C_6H_3$-4-CHO)(PPh_3), 4a: 90% yield. Anal. Calcd for $C_{25}H_{19}IrNO_4P$: C, 48.38; H, 3.08; N, 2.25. Found: C, 49.00; H, 2.97; N, 2.19.

Ir(NO)(1,2-$O_2C_6H_3$-4-$COOCH_3$)(PPh_3), 5a: 85% yield. Anal. Calcd for $C_{26}H_{21}IrNO_5P$: C, 47.99; H, 3.25; N, 2.15. Found: C, 47.12; H, 3.30; N, 2.09.

Ir(NO)(1,2-$O_2C_6H_3$-4-CH_2OH)(PPh_3), 6a: 70% yield. Anal. Calcd for $C_{25}H_{21}IrNO_4P$: C, 48.22; H, 3.39; N, 2.24. Found: C, 48.70; H, 3.32; N, 2.19.

Ir(NO)(1,2-$O_2C_6H_4$)(PPh_3), 7a: 70% yield. Anal. Calcd for $C_{24}H_{19}IrNO_3P$: C, 48.64; H, 3.23; N, 2.36. Found: C, 49.21; H, 3.16; N, 2.41.

Equilibrium Constant Determination. Apparatus. Infrared spectra were recorded using a Perkin-Elmer 180 (4000–180 cm^{-1}) instrument and a OrielOptik variable-temperature cell with KBr windows spaced at 0.5 mm.

Materials. Reagent grade 1,2-dichloroethane was distilled from calcium chloride and stored over molecular sieves and under argon. Reagent grade triphenylphosphine (Strem Chemicals) was recrystallized from benzene–ethanol before use. Tetracoordinate complexes were recrystallized from diethyl ether–hexane before use.

Procedure. The values of K_{eq} for the general association tetracoordinate + PPh_3 $\rightleftarrows$ pentacoordinate reaction at 30 ± 1 °C were calculated on the basis of the equilibrium concentration values of the tetracoordinate species, obtained by infrared measurements of the nitrosyl ligand stretching band intensity. For all the different tetracoordinate samples a good linear dependence, between the band area and the sample concentration, in the range employed was verified. The area, using the triangular approximation, has been equated to the height multiplied by the width at half-height. In order to calculate the K_{eq} values for each tetracoordinate complex, three sample solutions having the same complex concentration (10^{-3} M in 1,2-dichloroethane)

Table I. Infrared Stretching Frequencies of the Nitrosyl Group in Iridium-Catecholato Complexes[a]

		ν(NO), cm^{-1}	
no.	compound	tetracoordinate	pentacoordinate
1a	$Ir(NO)(1,2\text{-}O_2C_6Cl_4)(PPh_3)$	1861	
1b	$Ir(NO)(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2$		1597
2a	$Ir(NO)(1,2\text{-}O_2C_6Br_4)(PPh_3)$	1860	
2b	$Ir(NO)(1,2\text{-}O_2C_6Br_4)(PPh_3)_2$		1595
3a	$Ir(NO)(1,2\text{-}O_2C_6H_3\text{-}4\text{-}NO_2)(PPh_3)$	1857	
3b	$Ir(NO)(1,2\text{-}O_2C_6H_3\text{-}4\text{-}NO_2)(PPh_3)_2$		1593
4a	$Ir(NO)(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CHO)(PPh_3)$	1852	
4b	$Ir(NO)(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CHO)(PPh_3)_2$		1588
5a	$Ir(NO)(1,2\text{-}O_2C_6H_3\text{-}4\text{-}COOCH_3)(PPh_3)$	1850	
5b	$Ir(NO)(1,2\text{-}O_2C_6H_3\text{-}4\text{-}COOCH_3)(PPh_3)_2$		1584
6a	$Ir(NO)(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2OH)(PPh_3)$	1845	
6b	$Ir(NO)(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2OH)(PPh_3)_2$		1581
7a	$Ir(NO)(1,2\text{-}O_2C_6H_4)(PPh_3)$	1844,[a] 1848[b]	
7b	$Ir(NO)(1,2\text{-}O_2C_6H_4)(PPh_3)_2$		1576[b]
8a	$Ir(NO)(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_3)(PPh_3)$	1841[a], 1837[b]	
8b	$Ir(NO)(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_3)(PPh_3)_2$		1561[b]

[a] In 1,2-dichloroethane solution at 30 ± 1 °C. [b] KBr pellets.

and a molecular ratio with triphenylphosphine of 1:0.8, 1:1.0, 1:1.2, respectively, were prepared. The so calculated log K_{eq} values fell in a ±0.05 range with respect to the averaged value reported in Table II. After triphenylphosphine addition, all the tetracoordinate complex solutions reached immediately the equilibrium and then no change in intensity of the nitrosyl band was observed during 30 min. In the same time no bands attributable to decomposition products or byproducts were present. All measurements were performed after equilibrating the solutions for 15 min at 30 ± 1 °C.

Results and Discussion

In a previous paper we have reported the preparation and characterization of pentacoordinate and tetracoordinate *o*-quinone–nitrosyl complexes of rhodium and iridium by reaction between a dicationic metal–nitrosyl complex and tetrahalocatechols or tetrahalo-*o*-quinones, respectively.[8] Infrared evidence has shown that these pentacoordinate complexes undergo a slight phosphine dissociation to form the corresponding tetracoordinate complex. Further experiments carried out in this field in our laboratory have then shown that in the iridium case, tetracoordinate nitrosyl complexes can be obtained also by reaction between $Ir(NO)(CH_3CN)_2(PPh_3)_2^{2+}$ and sodium salts of catechols having electron-withdrawing ring substituents.[7] These results are a further support to the existence of the tetracoordinate–pentacoordinate equilibrium. The solubility of the two species plays a certain role during the formation process. In fact, depending on the reaction solvent volume and independent from the electronic effect of the ring substituents, we were always able to isolate the pentacoordinate species as a crude product. The tetracoordinate species can then be obtained by reaction of the corresponding pentacoordinate complex and chloranil as reported in the Experimental Section. The tetracoordinate- and pentacoordinate-characterized complexes and their ν(NO) stretching frequencies are reported in Table I.

It is noteworthy to underline that we are dealing with two series of isostructural and isoelectronic tetracoordinate and pentacoordinate complexes, the only difference being the catecholato ring substituents. While to the tetracoordinate complexes a d^8 configuration can be assigned, the drastic change on the ν(NO) stretching frequency, about 265 wavenumbers on going to pentacoordination, would suggest for this case a formal d^6 configuration. Recently, during studies devoted to the understanding of the changes in coordination number from 4 to 5 in d^8 complexes, Halpern has reported the equilibrium association reaction of the iridium(I) complex $IrCl(CO)(PMe_2Ph)_2$ with free PMe_2Ph.[9] Earlier, Collman et al. had studied the equilibrium formation reaction of $IrI(CO)_2(PPh_3)_2$ by interaction of the iridium(I) complex $IrI(CO)(PPh_3)_2$ and free carbon monoxide;[10] the tendency of the formation of the pentacoordinate species is greater for the iodide complex when compared with that of the corresponding chloride complex; the same behavior trend has been found by Vaska in the formation of the molecular oxygen derivative.[11] In this paper we report the determination of the equilibrium constants K_{eq} for reaction 1. The equilibrium constant values

Table II. Equilibrium Constants for the Reaction[a] tetra + $PPh_3 \rightleftarrows$ penta Compared with $K_a{}^I$ of the Corresponding Free Catechols[b]

reaction	log K_{eq}	p$K_a{}^I$
1a + $PPh_3 \rightleftarrows$ **1b**	3.39	6.63
2a + $PPh_3 \rightleftarrows$ **2b**	3.27	
3a + $PPh_3 \rightleftarrows$ **3b**	2.96	7.65
4a + $PPh_3 \rightleftarrows$ **4b**	2.36	8.30
5a + $PPh_3 \rightleftarrows$ **5b**	2.11	
6a + $PPh_3 \rightleftarrows$ **6b**	1.56	
7a + $PPh_3 \rightleftarrows$ **7b**	1.40	10.91
8a + $PPh_3 \rightleftarrows$ **8b**	1.06	11.30

[a] In 1,2-dichloroethane solution at 30 ± 1 °C. tetra = tetracoordinate complex; penta = pentacoordinate complex. [b] From ref 16.

$$Ir(NO)(cat)(PPh_3) + PPh_3 \rightleftarrows Ir(NO)(cat)(PPh_3)_2 \qquad (1)$$

(see Table II) have been calculated by IR measurements by adding different amounts of triphenylphosphine to solutions of the tetracoordinate complexes and following the intensity decrease of the corresponding well-defined band of ν(NO) stretching. The use of the tetracoordinate species as starting complexes is due to the fact that these compounds can be easily purified and recrystallized to eliminate all possible traces of free triphenylphosphine. The measurements have been carried out in 1,2-dichloroethane solution, because this solvent is able to ensure the complete solubility of the less soluble pentacoordinate species in our experimental conditions. The tetracoordinate:triphenylphosphine molar ratio used has been chosen in such a way that the lower limit of triphenylphosphine concentration was enough to set the equilibrium in an IR-detectable position and to ensure that the upper limit of the triphenylphosphine concentration was not sufficiently high for by-product reactions (i.e., the formation of $Ir(NO)(PPh_3)_3$[7]) to take place.

From the present knowledge of the metal–phosphorus bond formation and stability[12] the occurrence of associative equilibrium reaction 1 must depend on the actual electron density present on the central metal. As said before, the tetracoordinate complexes of the type $Ir(NO)(cat)(PPh_3)$ have a d^8 electronic configuration, which leads to a nitrosyl group linearly bonded; therefore, in this case, the nitrosyl ligand is isoelectronic with the carbonyl group. However, it is well-known that the metal carbon in the carbonyl case is sensitive to the electron density on the metal and that in a homogeneous series of compounds the ν(CO) stretching frequencies can be good indication of the metal electron density situation.[13,14] Thus, it is reasonable to suppose the same behavior for the nitrosyl group in these series of catecholato complexes. In Figure 1 is reported the plot of the log of the equilibrium constants, log K_{eq}, vs. the ν(NO) stretching frequencies of the tetracoordinate species involved in the equilibrium reaction. The dependence is strictly linear, showing that to higher ν(NO) stretching frequencies there are correspondingly higher values for the equilibrium constants and consequently lower electron density on the metal. The Figure 1 plot, built up using equilibrium constants relative to a large number of equilibrium reactions and frequency data relative to the isoelectronic and isostructural nitrosyl catecholato tetracoordinate complexes involved in these reactions, proves that the ν(NO) stretching

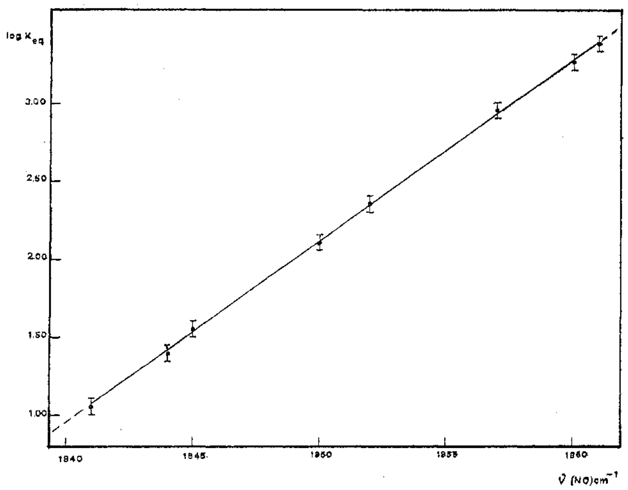

Figure 1. Plot of log K_{eq} vs. ν(NO) of the tetracoordinate complexes.

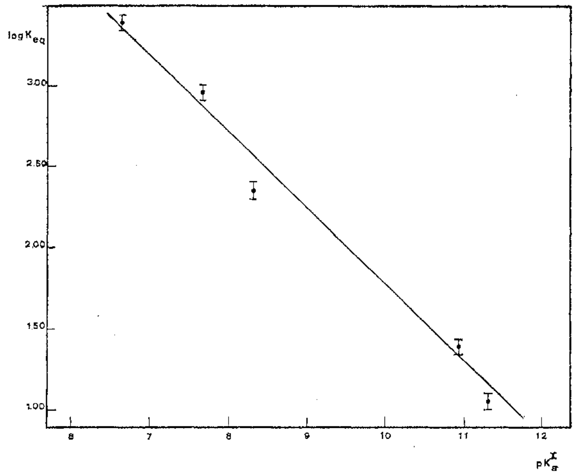

Figure 2. Plot of log K_{eq} vs. p$K_a{}^I$ of the free catechols.

frequency is a good test of the relative electronic situation on the metal in such classes of complexes. Recalling that the catechol ring substituents are the only composition differences between the complexes, it is possible to note from Table II that the trend of the equilibrium constant parallels the electron-withdrawing or -releasing power of the ring substituents. This effect is evidently visualized in the comparison of the tetrachloro derivative's equilibrium constant, **1a** + $PPh_3 \rightleftarrows$ **1b**, with that calculated for the unsubstituted catechol derivative's case, **7a** + $PPh_3 \rightleftarrows$ **7b**, which is lower for a 10^2 term. Consequently, this means that the electronic effect, induced by the catechol ring substituent, is largely felt by the metal. Earlier, Balch, Röhrsheid, and Holm had suggested that in such species having a quinonoid ligand three different formulations related by one-electron transfer should exist[15] and that then the oxygen atoms could be considered to act as electron bridges between the ring and the metal. The bridge effectiveness and the electron transfer are, in our case, determined by the electron-withdrawing or -releasing power of the ring substituents. Thus, the values of the equilibrium constants can be taken as a measure of the actual electron density on the metal. Because the electronic effect of the ring substituents in the uncoordinated catechols can be measured by the values of the corresponding first dissociation constants,[16] $K_a{}^I$, a plot of the equilibrium constants, log K_{eq}, vs. p$K_a{}^I$ for the corresponding catechols gives a quantitative correlation between the ring substituent's influence and the equilibrium constants. From Figure 2 it is possible to see that this dependence is linear.

The knowledge of this dependence gives the possibility to tailor complexes with a predetermined relative electron density on the metal starting from a catechol derivative with an appropriate $K_a{}^I$. Our interest in these studies is strictly correlated to the potential use of the d^8 complexes of this type (i.e., containing two ligands with empty π orbitals at low energy) as homogeneous catalysts. The structure of the active species, as well as that of all intermediates involved in the catalytic cycle, must be established in order to study the various factors influencing catalytic behavior. Unfortunately, such intermediates are often too unstable to isolate, and indirect evidence of their existence must be relied on; few systems have been so thoroughly investigated as to establish a general acceptance rule. Moreover, it is well-known that a catalyst's activity and selectivity depend on a number of properties which change from species to species; meaningful comparison of catalyst activity and selectivity can be made only between those complexes with isoelectronic structures and identical coordination numbers and modifying ligands. For catalysts of the type $MX(CO)L_2$ (with M = Rh, Ir; X = Cl, Br, I; L = tertiary phosphine or phosphite), the literature reports qualitative estimates of the electron density obtained by the variation of the ν(CO) stretching frequency as a function of the different ligands.[17] Wilkinson and co-workers have found that in ruthenium hydridocarboxylato complexes a change in the carboxylato group has an effect on the rate of hex-1-ene, hydrogenation being faster with electron-releasing carboxylato groups.[18] Consequently, the study reported in this paper should be considered as a further step contributing to the deeper knowledge of the mechanism operating in a catalytic cycle in order to develop a general acceptable rule.

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Registry No. 1a, 62521-03-3; **1b**, 66609-61-8; **2a**, 62521-04-4; **2b**, 66609-62-9; **3a**, 66551-70-0; **3b**, 65521-10-0; **4a**, 66551-71-1; **4b**, 65521-11-1; **5a**, 66551-72-2; **5b**, 65521-12-2; **6a**, 66551-73-3; **6b**, 66551-74-4; **7a**, 65531-59-1; **7b**, 66551-75-5; **8a**, 65531-60-4; **8b**, 66551-76-6; $Ir(NO)(CH_3CN)_2(PPh_3)_2{}^{2+}$, 59983-14-1.

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