groups is taken to be that of 1-hexene.[2c] The very large drop in K_1 on increasing n from 0 to 1 is attributed to blocking resonance interaction between the olefin and cyano groups. The smaller subsequent effect of increasing chain length is attributable to a diminishing inductive effect. Surprisingly, the CN group still has a pronounced effect on K_1 even when separated from the double bond by three methylene units. That this effect is electronic can be seen by the steady increase in λ_{max} and λ_{sh} of the (Ol)NiL_2 complexes with increasing n in Table V. Values for 1-hexene are 354 and 392 nm.

The nitrile complex formation constant $K_N = 190$ for the nonconjugated cyanoolefin 3PN is essentially the same as that found for the alkanenitriles[3] suggesting that the isolated C═C has little effect on nitrile coordination. The conjugated cyanoolefins C2PN and T2M2BN, however, show larger values of $K_N \approx 450$. The larger K_N is attributed to electron delocalization effects. This conclusion is supported by the shift in the longest wavelength electronic transition from ~300 nm in the (RCN)NiL_3 complexes with alkanenitrile to ~370 nm with conjugated cyanoolefins. Benzonitrile, which has a larger delocalized π system, shows a further shift of λ_{max} to 396 nm and an increase in K_N to ~10^3.[3]

The ^{31}P NMR chemical shifts of the (RCN)NiL_3 complexes (Table I) are found in a narrow and characteristic range; there is, however, a tendency for the conjugated nitrile complexes to give resonances at slightly lower fields.

Cyanoolefins represent a type of ambidentate ligand that can bond in more than one way. Numerous complexes of acrylonitrile have been described, some of which are olefin and some nitrile bonded.[17] For example, acrylonitrile has been shown to be nitrile bonded in (ACN)$W(CO)_5$ and olefin bonded in $(ACN)_3W(CO)_3$. To our knowledge, however, our work on cyanoolefins is the first to show the presence of both olefin and nitrile complexes in equilibrium in solution and to determine equilibrium constants which provide a complete description of the system.

Acknowledgment. I am indebted to Drs. F. J. Weigert and C. M. King for samples of cyanoolefins and to Mrs. Adah B. Richmond for chromatographic separations. Thanks are also owed to Dr. P. Meakin for assistance with the ^{31}P spectra and Mr. D. W. Reutter for the spectrophotometric work. Helpful discussions with Dr. W. C. Seidel are gratefully acknowledged.

Registry No. NiL_3, 28829-00-7; $BNiL_2$ (B = styrene), 41685-58-9; $BNiL_3$ (B = acetonitrile), 33270-65-4; $BNiL_3$ (B = valeronitrile), 33270-67-6; $BNiL_3$ (B = adiponitrile), 41686-93-5; $(C_6H_5CN)NiL_3$, 33270-68-7; (p-FC_6H_4CN)NiL_3, 41686-99-1; (ACN)NiL_2, 31666-48-5; (3BN)NiL_3, 84521-37-9; (3BN)NiL_2, 84521-38-0; (2M3BN)NiL_3, 41686-95-7; (2M3BN)NiL_2, 84521-39-1; (4PN)NiL_3, 41852-92-0; (4PN)NiL_2, 84521-40-4; (T2PN)NiL_3, 84620-19-9; (T2PN)NiL_2, 84521-41-5; (T3PN)NiL_3, 84581-09-9; (C2M2BN)NiL_3, 84521-42-6; [(5HN)NiL_2], 84521-43-7; [(T3PN)NiL_2], 84521-44-8; [(C2PN)NiL_3], 84620-20-2; [(C2PN)NiL_2], 84581-10-2; C_6H_5CN, 100-47-0; P-FC_6H_4CN, 1194-02-1; ACN, 107-13-1; 3BN, 109-75-1; 2M3BN, 16529-56-9; 4PN, 592-51-8; T2PN, 26294-98-4; T3PN, 16529-66-1; C2M2BN, 20068-02-4; 5HN, 5048-19-1; C2PN, 25899-50-7; acetonitrile, 75-05-8; valeronitrile, 110-59-8; adiponitrile, 111-69-3.

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Metalation-Resistant Ligands: Some Properties of Dibenzocyclooctatetraene Complexes of Molybdenum, Rhodium, and Iridium

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The chelating diolefinic ligand dibenzo[*a,e*]cyclooctatetraene (dct) displaces 1,5-cyclooctadiene (cod) from $[Ir(cod)Cl]_2$ to give $[Ir(dct)Cl]_2$. This reacts with $AgBF_4$ and PPh_3 to give $[Ir(dct)L_2]BF_4$. The addition of H_2 at −80 °C gives *cis*-$[IrH_2(dct)L_2]BF_4$, which is stable at 20 °C in CH_2Cl_2 but rearranges with methanol catalysis at −30 °C to *cis,trans*-$[IrH_2(dct)L_2]BF_4$. This appears to be the first case of such a catalyzed rearrangement and takes place by a deprotonation/reprotonation sequence. The intermediate $[IrH(dct)L_2]$ can be obtained from the cis,trans dihydride and *t*-BuOK. Where L_2 is 1,3-bis(diphenylphosphino)propane (dpp), a cis dihydride is obtained at −80 °C, which rearranges with methanol catalysis to a new trans isomer. The analogous rhodium complex $[Rh(dct)L_2]PF_6$ (L = PPh_3) does not react with H_2, but $[RhH_2(dct)L_2]PF_6$, the first rhodium dihydride olefin complex, can be obtained from dct and $[RhH_2(Me_2CO)_2L_2]PF_6$. The strongly electrophilic character imparted to its complexes by the dct ligand is discussed with reference to the IR of (dct)$Mo(CO)_4$ which suggests that dct is substantially more electron-withdrawing than cod. A Tolman-type electronic parameter for both monodentate and chelating ligands is proposed. The substitution of dct for cod makes the complex *cis,trans*-$[IrH_2(diene)(PPh_3)_2]BF_4$ more acidic by at least 8 p*K* units.

Introduction

Over the last few years, we have been trying to develop transition-metal complexes as homogeneous systems for the selective activation of CH bonds, especially of alkanes.[1] We expected intramolecular cyclometalation[2] of ligand CH bonds to occur to the exclusion of intermolecular alkane activation. For this reason, in 1977 we set about the construction of metalation resistant ligands (see below). In 1979, we were surprised to find that alkane activation could occur[3] even in systems that can cyclometalate. More

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[2] Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977,** *89,* 75. K. Omae, I. *Coord. Chem. Rev.* **1980,** *32,* 235.

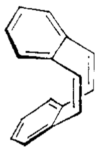

Figure 1. The conformation of free dct.

recently, other such systems have been found.[4] Clearly cyclometalation may be reversible in these systems and merely compete with alkane activation. It seems probable that more efficient activation could result if ligands resistant to cyclometalation could be used. In this paper we return to the question of metalation-resistant ligands, because we think that progress in this area may lead to significant advances in alkane activation.

Ligands tend to cyclometalate more readily in bulky systems where a stable ring can be formed. For phosphorus ligands the tendency to cyclometalate increases as $PMe_3 < PPh_3 < P(OPh)_3$.[2] A general method we are attempting to use to prevent cyclometalation is the construction of a ligand having a conformation that prevents the formation of a internally cyclometalated product.

In this paper we report some of the chemistry of dibenzocyclooctatetraene (1, dct), a tub-shaped molecule (Figure 1), which we hoped would be metalation-resistant by virtue of its lack of allylic hydrogens.

We first looked at the donor/acceptor properties of dct by IR spectroscopy of the tetracarbonyl molybdenum derivatives. We then examined some iridium and rhodium complexes of dct, the corresponding 1,5-cyclooctadiene (cod) chemistry of which we had already studied:[5] striking differences were observed.

Results and Discussion

Dibenzocyclooctatetraene (1) has been obtained by several routes[6,7] and has been shown to bind to transition metals.[7] The synthesis we have used[7] gives ca. 25% yield of dct from $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene, but it is inconvenient involving a $Ni(CO)_4$-mediated coupling and a pyrolysis. Dct is also commercially available. X-ray crystallography shows that dct adopts in the tub conformation[8] (Figure 1). This must also be the conformation in which dct binds to a metal. Force-field calculations[9] suggest that free cod adopts the twist-boat conformation, with the chair being only slightly (1.3 kcal/mol) higher. The C_{2v} boat, like that for dct, is less stable, probably due to eclipsing interactions in the allylic CH_2 groups.

For these reasons alone, dct might be expected to be a much better ligand than cod. Another contributing factor is the aryl substituent on the C=C bond. An arene ring is electron withdrawing in the σ framework and electron donating in the π framework. In dct, the aryl rings are twisted relative to the C=C bond in such a way as to decouple the π effect, leaving only the σ effect. The increase in electron-acceptor behavior on going from cod and dct is therefore expected to be substantial. We wished to form some idea of the magnitude of this effect.

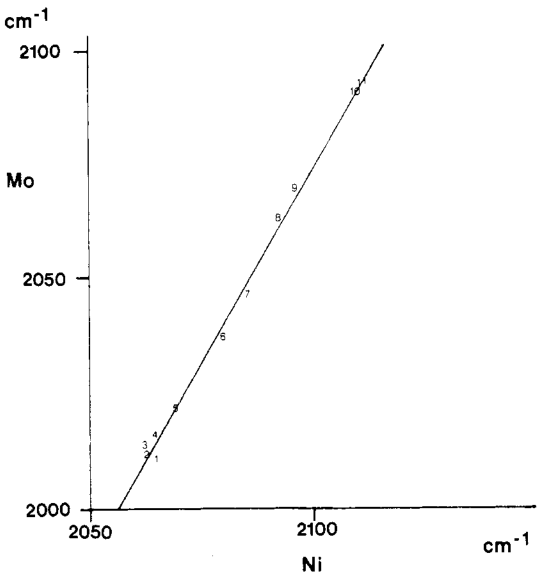

Figure 2. The electronic parameter ν_{Mo} plotted against Tolman's parameter ν_{Ni}. Identifying labels are as follows: 1, PMe_2Ph; 2, PEt_2Ph; 3, PEt_3; 4, PMe_3; 5, PPh_3; 6, $P(OMe)_3$; 7, $P(OPh)_3$; 8, $PCl_2(OEt)$; 9, PCl_3; 10, PF_3; 11, $P(CF_3)F_2$.

Tolman[10] has compared the electronic effects of various monodentate ligands by using the A_1 ν(CO) vibration of $LNi(CO)_3$. Chelating ligands cannot be studied with $LNi(CO)_3$, so we searched for a more suitable system. *cis*-$Mo(CO)_4L_2$ seems to fit the requirements. These are easily made, air-stable complexes, and both chelating and monodentate ligands can be studied.[11,12] Literature data are available for many derivatives of this type.[12] Further advantages of the Mo system are the greater convenience and much lower toxicity of $Mo(CO)_6$ relative to $Ni(CO)_4$ and the wider range of ligands L that bind, including N, O, and S donor ligands. The halide ions can also be used in this system. We adopted the same criterion as Tolman, using the highest frequency (A_1) vibration for comparison. The normal mode associated with this vibration mainly involves the pair of trans CO groups, but the bands are always strong enough to be easily observed and assigned.

In Figure 2, the molybdenum and nickel parameters are compared for 11 phosphorus ligands of various types for which data are available. The correlation coefficient is 0.996, showing that the parameters are very close agreement in measuring the same property of the ligands, presumably their overall donor power. The slope of the graph (1.69) shows that the molybdenum parameter has the advantage of being more sensitive. This is probably due to the presence of two L ligands in the Mo case (0.5 L/CO) compared to one L in the Ni case (0.33 L/CO). For convenience, the equation connecting the Tolman parameter ν_{Ni} with the present parameter ν_{Mo} is given below (eq 1).

$$\nu_{Ni} = 0.593\nu_{Mo} + 871 \qquad (1)$$

We have made $(cod)Mo(CO)_4$ and $(dct)Mo(CO)_4$ by literature methods[11] and have measured their IR spectra in pentane solution. Comparing these with other values

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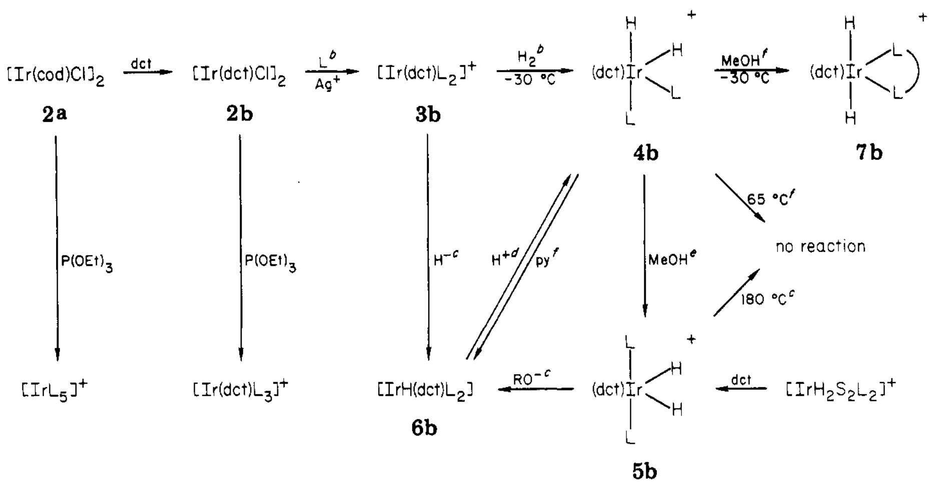
Scheme I. Some Reactions of the Iridium Complexes[a]



[a] cod = 1,5-cyclooctadiene; dct = dibenzocyclooctatetrene; S = Me$_2$CO; py = pyridine. [b] L = PPh$_3$, PMePh$_2$, 0.5dpe, or 0.5dpp. [c] L = PPh$_3$. [d] L = PPh$_3$ or 0.5dpp. [e] L = PPh$_3$ or PMePh$_2$. [f] L = 0.5dpp.

found for *cis*-[$L_2Mo(CO)_4$] complexes in the literature gives the following order of donor strength: PCl_3 (2072) < dct (2052) < $P(OPh)_3$ (2046) < cod (2038) < $P(OMe)_3$ (2037) < PPh_3 (2022).

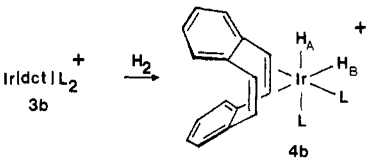
This strong electron-acceptor character of dct relative to cod probably helps increase the strength of the metal–olefin bonding and accounts, together with the factors mentioned above, for the exceptionally strong bonding we observed between dct and rhodium and iridium (see below).

We wished to see whether the electron-withdrawing properties of dct would enhance the electrophilic character we have found for a variety of cod complexes of rhodium and iridium[13] and were therefore interested in the synthesis of [Ir(dct)Cl]$_2$.

1 (dct) reacts smoothly with [Ir(cod)Cl]$_2$ (**2a**) in CH_2Cl_2 to give a bright yellow solution and microcrystalline precipitate of the corresponding [Ir(dct)Cl]$_2$ (**2b**).[14] Additional **2b** was precipitated with hexane. In contrast with the cod analogue, **2b** is air stable both in the solid and in solution. The ^1H NMR and IR spectra are consistent with the proposal that dct binds as a chelating diolefin like cod. In particular, the ν(C=C) vibration at 1646 cm^{-1} in the IR spectrum of dct is shifted to 1603 cm^{-1} on coordination, and δ(CH) vinyl is shifted from δ 6.8 to δ 5.33, as expected[15] for this structure. Other cases are known in which dct binds in an η^4 fashion,[7] but η^6 binding to the aromatic ring has been reported only for the $Cr(CO)_3$ group.[11]

The product is relatively insoluble, in contrast to **2a**, and recrystallization is therefore difficult. We find, however, that **2b** dissolves in CH_2Cl_2 in the presence of C_2H_4, presumably to form (dct)IrCl$(C_2H_4)_x$ (x = 1 or 2). Ethylene is readily lost over several hours or more rapidly on purging with N_2, and pure **2b** crystallizes from the solution.

As expected **2b** reacts with PPh_3 and $AgBF_4$ in CH_2Cl_2 to give [(dct)IrL$_2$]BF$_4$ (**3b**) (L = PPh_3) after removal of the AgCl formed. The complex can be isolated with hexanes to give a CH_2Cl_2 solvate or can be recrystallized from CH_2Cl_2/MeOH to give the mixed MeOH/CH_2Cl_2 solvate. The ^1H NMR spectrum supports the formulation. The phenylene ring protons absorb at δ 6.8 and 7.0, as expected for uncoordinated groups, and the cod vinyl protons at δ 4.7. In the case of **3b**·CH_2Cl_2·MeOH, free MeOH at δ 3.3 can also be seen. In each case free CH_2Cl_2 at δ 5.3 is seen. At −80 °C **3b**·CH_2Cl_2 adds H_2 to give the expected *cis*-[(dct)IrH$_2$L$_2$]BF$_4$, which is the only product that can be detected by ^1H NMR spectroscopy (eq 2 and Scheme I).



(2)

H_A appears as a doublet of doublets at δ −7.5 and H_B as a triplet at δ −12.75. While H_B appears in almost exactly the same place (δ −12.63) in the cod analogue[5] **4a**, H_A is shifted 2.2-ppm downfield (**4a**, δ −9.7; **4b**, δ −7.52).

The solution of **4b** can be warmed to room temperature without either loss of the H_2 or transfer to and hydrogenation of the olefin ligand; **4a** does both above −20 °C. At 80 °C H_2 is lost, but dct hydrogenation still does not occur. Indeed we have found no conditions under which dct can be hydrogenated homogeneously. This presumably arises from the strength of the dct–metal bond and the rigidity of dct itself. Models show that one C=C group of coordinated dct cannot insert into an M–H bond without the second C=C group becoming detached. This effect means that dct is a permanently bound ligand like PPh_3 not subject to hydrogenation rather than a ligand such as cod, which can be hydrogenated.

In contrast to the behavior found for **3b**·CH_2Cl_2, a sample of the dihydride **4b** formed at −80 °C from **3b**·CH_2Cl_2·MeOH, rearranged on warming to −30 °C. The product was *cis,trans*-[Ir(dct)H$_2$L$_2$]BF$_4$, **5b**, as shown by ^1H NMR spectroscopy. A triplet at δ −12.6 is assigned to the IrH groups and a triplet at δ 5.2 to the dct vinyls. By ^{13}C NMR spectroscopy the vinyl carbon appears as a singlet at 89.8 ppm, showing[16] the dct is cis to the L groups and confirming the cis,trans structure. Both the cis (**4a**) and cis,trans (**5a**) isomers are known in the case of cod, but they do not interconvert under any conditions we have studied. We inferred that the rearrangement was catalyzed by MeOH in the dct case and confirmed this by adding MeOH (1 equiv/Ir) to a sample of **4b** at 0 °C formed from

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[14] Compounds are numbered **a** for cod derivatives and **b** for dct derivatives.

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Table I. ^1H NMR Data for the New Complexes[a]

complex	aryl	vinyl	hydride	other resonances
$[Ir(dct)Cl]_2$	6.9, c	5.33, s		
$[Ir(dct)(PPh_3)_2]BF_4$	7.0, c 6.8, c	4.7, br		
cis-$[IrH_2(dct)(PPh_3)_2]BF_4$[b]	6.7, c	4.4, t (8) 5.2, t (7) 5.4, c 5.8, d (8)	−7.5, dd (19, 83) −12.75, t (15)	
cis,trans-$[IrH_2(dct)(PPh_3)_2]BF_4$	6.7, c 6.3, c	5.2, t (3)	−12.5, t (14)	
$[IrH(dct)(PPh_3)_2]$	6.6, c	4.65, d (12)	−13.7, t (21)	
$[Ir(dct)(dpe)]PF_6$	7.5, br 6.9, br	5.4, s		2.5, c, CH_2
cis-$[IrH_2(dct)(dpe)]PF_6$[b]	7.4, br 7.1, br	6.1, br 5.2, br 4.7, br	−7.5, dd (16, 85) −13.5, t (16)	3.1, br, CH_2
$[Ir(dct)(dpp)]PF_6$	7.7, br 7.2, br 7.1, br	5.2, s		3.1, br, CH_2 2.4, br, CH_2
cis-$[IrH_2(dct)(dpp)]PF_6$[b]	7.7, br 7.1, br 6.8, br 6.6, br	6.3, br 6.0, br 5.0, br 4.8, br		3.3, br, CH_2 2.9, br, CH_2 1.4, br, CH_2
trans-$[IrH_2(dct)(dpp)]PF_6$	7.4, br 6.8, br	4.3, br	−5.9, t (17)	3.4, br, CH_2 1.4, br, CH_2
$[Ir(dct)(PMePh_2)_2]PF_6$	7.3, c 6.8, c 6.6, c	5.1, t (3)		2.3, t (4), Me
trans-$[IrH_2dct(PMePh_2)_2]PF_6$	6.8, c	5.1, t (14)	−13.2, t (15)	2.3, t (14), Me
$[Ir(dct)(P\{OEt\}_3)_3]PF_6$	6.8, s	4.6, q (1)		4.1, c, CH_2 1.3, t, Me
$[Rh(dct)Cl]_2$	6.9, br	5.0, d (2)		
$[Rh(dct)(PPh_3)_2]PF_6$	7.1, c 6.8, c	5.1, br		
cis,trans-$[RhH_2(dct)(PPh_3)_2]PF_6$[b]	7.1, c 6.7, c	5.3, br		−12, c

[a] Spectra recorded at 25 °C in $CDCl_3$ (except where noted) and reported as position (δ, relative to internal Me_4Si), multiplicity (coupling constant in hertz): c, complex; br, broad; d, doublet. [b] At −80 °C in CD_2Cl_2.

3b·CH_2Cl_2. Rearrangement was effectively instantaneous at room temperature. Even atmospheric moisture was capable of promoting the rearrangement.

The mechanism of this rearrangement is most probably a deprotonation/reprotonation sequence. Addition of MeOD leads to **5b**-d_2 in which the H ligands have been completely exchanged. Exchange does not occur below the rearrangement temperature, however.

The postulated monohydride intermediate $[IrH(dct)L_2]$ (**6b**) can be made by the acton of *t*-BuOK on *cis,trans*-$[IrH_2(dct)L_2]$ (**5b**) or less conveniently by reaction $LiBEt_3H$ on $[Ir(dct)L_2]BF_4$. The product is a colorless microcrystalline solid and, like the cod analogue **6a**, is fluxional in solution on the ^1H NMR time scale (see Table I). Protonation (CF_3CO_2H, −80 °C) gave a solution in which only the cis dihydride **4b** could be observed (NMR). This implies that multiple deprotonation/reprotonation steps are required to convert **4b** to **5b**, since one cycle would largely reform the cis isomer **4b**. An alternative possibility is that **5b** is only formed by protonation of **6b** above −30 °C. The most reasonable[17] structure for the monohydride is shown in Figure 3. Of the three possible positions at which protonation can take place (marked with arrows) two lead to the cis and one to the *cis,trans* isomers. Possibly the approach of the acid is kinetically determined by the steric bulk of L, or there may be a preference to attack trans to L the ligand of lowest trans effect.

This appears to be the first case of a metal hydride rearrangement going to a deprotonation/reprotonation equilibrium and shows the influence that weak bases such as water or methanol can have on reactions of metal hydrides.

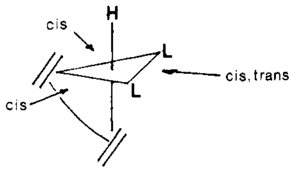

Figure 3. Protonation of $IrH(dct)L_2$ to give *cis-* or *cis,trans*-$[IrH_2(dct)L_2]^+$.

We have pointed out[18a] that cod complexes such as **2a** are electrophilic or Lewis acid in their properties. Hydrogen addition tends to be reductive in this series, so that the hydrogen ligands of the adducts **4a** and **5a** tend to take on δ+ character. The additional electron-acceptor character of dct, compared to cod, enhances the electrophilic character of **3b** compared to **3a** to such a point that the dihydride **4b** distinctly acidic and can even partially protonate methanol. Since the cis dihydride **4b** converts to the cis,trans complex **5b** by deprotonation/reprotonation, **5b** must be the least acidic of the two. **5b** does not exchange with MeOD.[18b] In CD_2Cl_2 **5b** can be deprotonated by pyridine (2 molar equiv) but not by aniline (2 molar equiv), suggesting that pK_a[19] of the metal hydride is ca. 11. The cod analogue **5a** cannot be deprotonated even by NEt_3, suggesting it has a pK_a above 19.

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[17] Churchill, M. R.; Bezman, S. A. *Inorg. Chem.* **1972**, *11*, 2243.

[18] (a) Crabtree, R. H.; Hlatky, G. G. *Inorg. Chem.* **1980**, *19*, 571. Crabtree, R. H.; Quirk, J. M. *J. Organomet. Chem.* **1980**, *199*, 99. (b) This implies that both hydrides in **4b** must be MeOD exchangeable, since **5b**-d_2 is obtained above −30 °C.

[19] Based on pK_b values of the amines in CH_3CN (Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255).

cis,trans-$[IrH_2(dct)L_2]BF_4$ (**5b**) was also formed from $[IrH_2(Me_2CO)_2L_2]BF_4$ and dct in CH_2Cl_2, just as **5a** is obtained with cod.[5] While the cod analogue **5a** loses H_2 above 80 °C on heating, **5b** is stable at least to 180 °C in air or on reflux in $CHCl_3$ for at least 1 h. This degree of stability in a dihydrido olefin complex is striking and a further example of the electrophilic character of the metal. On classical ideas, electron-withdrawing substituents should destabilize an oxidative addition product; here, the electron-withdrawing dct stabilizes **4**, because the metal becomes more negative on H_2 addition. In short, the addition is reductive not oxidative as we have found in several related cases[18] (see below). No dct hydrogenation was observed in this system. In a future paper[20] we will discuss the use of dct as a selective hydrogenation-resistant poison for homogeneous catalysts in a test for the homogeneity of catalyst systems.

Complexes of Other Phosphine Ligands. Other complexes of type **3b** were also obtained as hexafluorophosphate[21] salts by the same method as mentioned above where L = $PMePh_2$, 0.5dpe, and 0.5dpp (dpe = 1,2-bis(diphenylphosphino)ethane; dpp = 1,3-bis(diphenylphosphino)propane). In the synthesis of $[Ir(cod)(dpe)]PF_6$, cod is relatively easily displaced and some $[Ir(dpe)_2]PF_6$ is formed unless care is taken. Dpe showed no tendency to displace the more strongly bound dct. The $PMePh_2$ case was very similar to that of PPh_3, in that only the cis,trans dihydride of type **5b** is observed in moist CH_2Cl_2 on passing H_2 at room temperature.

One unusual feature of $[Ir(dct)(PMePh_2)_2]PF_6$ was the ^1H NMR resonance of the PMe group. This showed full virtual coupling as would be expected for a trans complex. Occasionally virtual coupling of an intermediate type is observed for cis phosphines, as in $[Ir(cod)(PMePh_2)_2]PF_6$, but to our knowledge this is the first case where full virtual coupling has been observed.

The analogous complexes with the chelating phosphines behaved differently. **3b** (L = 0.5dpe) reacts with H_2 to give the cis adduct **4b**. No cis,trans complex of type **5b** is possible in this case nor is H_2 lost even on refluxing in $CHCl_3$ (65 °C) for 0.5 h. Nor does hydrogenation occur even though the stereochemistry enforces a coplanar M(C=C)H arrangement, the one most favorably to hydrogenation.[5]

In this case both the starting complex and the cis dihydride adduct are stable enough for ^{13}C NMR study. Two features of interest emerge. First, the addition of H_2 produces a large upfield shift of the C vinyl resonances in the C=C group of the dct ligand that is trans to the phosphine. We have interpreted such shifts in the cod analogues as suggesting that the addition of H_2 reduces the metal, rather than oxidizing it, as is commonly the case.[22] The shift here, 9.7 ppm, is over twice the shift in the corresponding cod series,[18] consistent with the greater electron-withdrawing character of dct compared with cod. These shifts must be affected to some degree by the change from four- to six-coordination of the attached metal ion, over and above the changes in electron density we are trying to estimate. In the case of dct, we can also study the corresponding quaternary carbons of the dct ligand. These should be much less affected by such extraneous factors. They too, are shifted upfield, in this case by 7.9 ppm. This also suggests that the H_2 addition indeed has reductive character and tends to confirm our interpretation.[18] In CD_2Cl_2, the dihydride can be deprotonated by pyridine (2 M equiv) but not by aniline, suggesting it has a pK_a of about 11.

The dpp case is different again. Here the cis dihydride is formed at −80 °C as shown by ^1H NMR spectroscopy (Table I), but on warming a complete and irreversible rearrangement takes place at 15 °C, or at 0 °C with $CF_3CO_2^-$ catalysis, to give a complex having a triplet hydride resonance at δ −5.63. The most reasonable structure for this complex is *trans*-$[IrH_2(dct)L_2]PF_6$ (**7b**) with mutually trans hydrides (Scheme I). An isomer of $[IrH_2(nbd)(PPh_3)_2]$ (nbd = norbornadiene) has been assigned the same configuration by Howarth et al.[23] The IrH resonance in this complex appears at δ −7.7, comparable with the value for **7b**. This assignment is confirmed for **7b** by the position of the ν(Ir–H) vibration in the IR spectrum at 1871 cm^{-1}. As Chatt[24] showed, this vibration is sensitive to the trans ligand. A band above 2000 cm^{-1} is expected and observed for all isomers except **7**, for which a much lower frequency is expected in view of the mutually trans hydride arrangement. The apparent trans addition of H_2 to $[Ir(dct)(dpp)]PF_6$ above 15 °C is therefore due to a cis addition followed by rearrangement.

It is not clear why a trans isomer is never observed for dpe unless **6b**, the monohydride intermediate, has an axial H, an axial–equatorial dpe, and a diequatorial dct, in which case only the cis isomer could reform on reprotonation.

Finally, we wished to see how strongly dct was bound by comparing the reactivity of $[Ir(diene)Cl]_2$ (**2**) with $P(OEt)_3$. At 80 °C, the cod complex **2a** quickly loses cod and $[Ir\{P(OEt)_3\}_5]^+$ is formed.[25] In contrast, **2b** can be refluxed in EtOH with $P(OEt)_3$ for 12 h without any loss of dct, $[Ir(dct)\{P(OEt)_3\}_3]^+$ being isolated in essentially quantitative yield. Some of these complexes (e.g., L_2 = dpe and L = $PMePh_2$) are very oxygen sensitive, apparently giving O_2 adducts. We are currently investigating these in more detail.

Rhodium Complexes. Cod reacts with $[RhH_2(EtOH)_2L_2]^+$ (L = PPh_3) to give only $[Rh(cod)L_2]^+$ and no trace of dihydrido olefin complex of type **4** or **5** even at low temperature.[26]

We find that dct (1 equiv/Rh) reacts with the rhodium solvent complex at −80 °C in CD_2Cl_2 to give *cis,trans*-$[RhH_2(dct)L_2]^+$. This is the first example of a dihydrido olefin complex of rhodium. The ^1H NMR spectrum is very similar to that of the iridium analogue **5b**, showing an RhH resonance at δ −12.0, a CH (vinyl) resonance at δ 5.3, as well as free EtOH (see Table I). On warming above −20 °C the hydride resonances decrease in intensity and the resonances of $[Rh(dct)L_2]^+$ smoothly replace those of the dihydrido olefin complex. This loss of H_2 seems to be irreversible, and we were unable to find any conditions under which H_2 would add to $[Rh(dct)L_2]^+$. The dihydride is therefore thermodynamically unstable with respect to $[Rh(dct)L_2]^+$, in sharp contrast to the corresponding Ir case, confirming the stronger binding of H_2 to Ir over Rh.

Conclusion

We have shown that dct is different from cod in several respects: (1) it is substantially more electron withdrawing; (2) it is hydrogenation resistant; and (3) it is more tightly

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bound. In future papers we will discuss the related properties of metalation resistance and resistance to nucleophilic attack.

The extra electrophilic character conferred on the metal by dct compared to cod is enough to make the metal hydrides sufficiently acidic to partially protonate methanol, leading to a new deprotonation/reprotonation mechanism for metal "hydride" rearrangements. The change in pK_a of the metal hydrides induced by a substitution of dct for cod is at least 8 units.

Experimental Section

NMR spectra were recorded on Brucker HX-270 and JEOL FX-90Q instruments and IR spectra on a Nicolet-7199 instrument. Standard Schlenk tube inert-atmosphere techniques were used. Dct,[7] (dct)$Mo(CO)_4$,[11] (cod)$Mo(CO)_4$,[11] and $[IrCl(cod)]_2$[27] were prepared by literature methods. Dct is also commercially available (ICN, K&K Labs).

Dichlorobis(η^4-dibenzo[*a*,*e*]cyclooctatetraene)diiridium(I). To $[Ir(cod)Cl]_2$ (820 mg) in CH_2Cl_2 (20 mL) was added dct (500 mg) in CH_2Cl_2 (20 mL) over 30 min. The solution was reduced to 10 mL in vacuo, and hexanes (25 mL) were added. The yellow product was filtered; yield 130 mg (65%). This was sufficiently pure for use in the preparations described below, but analytically pure material was only obtained after recrystallization as follows. A suspension of crude $[Ir(dct)Cl]_2$ (200 mg) in CH_2Cl_2 (20 mL) containing dct (20 mg) was prepared. Ethylene was passed until the complex dissolved and the excess C_2H_4 removed by passing N_2 briefly. Hexane (20 mL) was added carefully so that it formed a second layer above the CH_2Cl_2. After 20 h, pure microcrystalline $[Ir(dct)Cl]_2$ was formed: yield 130 mg (65%); IR (cm^{-1}, CH_2Cl_2 solution) 1603 (m), 1582 (m), 1490 (s), 1098 (m), 1002 (m), 831 (m). Anal. Calcd for $C_{16}H_{12}IrCl$: C, 44.49; H, 2.80. Found: C, 44.31; H, 2.84.

(Dibenzo[*a*,*e*]cyclooctatetraene)bis(triphenylphosphine)iridium(I) Fluoroborate. To a solution of $[Ir(dct)Cl]_2$ (100 mg, 0.22 mmol) and PPh_3 (120 mg, 0.44 mmol) in CH_2Cl_2 (20 mL) was added $AgBF_4$ (45 mg, 0.22 mmol). After 10 min of stirring, the resulting AgCl is filtered off, and the volume of the solution reduced to 15 mL. Hexanes and diethyl ether (3:1, 15 mL) were added to form a second layer. Red crystals of the product were deposited (1 day), filtered, and washed with Et_2O: yield 169 mg (76%); IR ($CDCl_3$, cm^{-1}) 3063 (m), 1597 (m), 1484 (s), 1434 (s), 1265, 1061 (vs); ^{13}C NMR ($CDCl_3$, reported as position δ from internal Me_4Si (multiplicity, coupling constant (Hz), assignment) 142.4 (complex, aryl), 85.9 (t, $^2J_{PC} = 5$, vinyl). Anal. Calcd for $C_{52}H_{42}IrP_2BF_4 \cdot CH_2Cl_2$: C, 58.25; H, 4.06. Found: C, 58.09; H, 4.22.

The methylene chloride–methanol solvate was prepared by dissolving the crude complex (100 mg) in $CH_2Cl_2/MeOH$ (4:1, 10 mL) and adding a second layer of hexanes. Red crystals of the product were formed in 1 day. Anal. Calcd for $C_{52}H_{42}IrP_2BF_4 \cdot MeOH \cdot CH_2Cl_2$: C, 57.65; H, 4.30. Found: C, 57.70; H, 4.19.

The $PMePh_2$ analogue was prepared in the same way in comparable yield.

***cis*-Dihydrido(dibenzo[*a*,*e*]cyclooctatetraene)bis(triphenylphosphine)iridium(III) Tetrafluoroborate.** $[Ir(dct)(PPh_3)_2]BF_4$ (100 mg) in CH_2Cl_2 (10 mL) at −80 °C was treated with H_2 (1 atm) until the red color was discharged. Et_2O (25 mL) was added at −80 °C, and white microcrystals were deposited, filtered cold, and dried: the ^1H NMR was recorded at −80 °C (Table I); IR (Nujol mull, cm^{-1}) 2181 (w), 2140 (w), 1054 (s), 752 (m), 695 (s). The complex had limited thermal stability and tended to rearrange to the cis,trans isomer in the presence even of weak bases.

***cis*,*trans*-Dihydrido(dibenzo[*a*,*e*]cyclooctatetraene)bis(triphenylphosphine)iridium(III) Tetrafluoroborate.** To *cis,trans*-$[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$ (250 mg) in CH_2Cl_2 (5 mL) was added dct (56 mg). After the solution was stirred for 30 min, Et_2O–hexane (1:1, 15 mL) was added as an upper layer. The crude product precipitated and was recrystallized by CH_2Cl_2/Et_2O–hexane bilayer diffusion, filtered, washed (Et_2O), and dried: yield 170 mg (65%) of colorless crystals; ^{13}C NMR ($CDCl_3$) δ 141.4 (c, Ar), 89.8 (s, vinyl); IR (CD_2Cl_2, cm^{-1}) 2182 (m), 1605 (m), 1481 (m), 1060 (vs), 1000 (m), 866 (m) 826 (m).

Observation of the H_2 Adducts. $[Ir(dct)L_2]BF_4$ (50 mg) was dissolved in CD_2Cl_2 in an NMR tube and cooled to −80 °C. H_2 was passed until the color of the solution was bleached. The ^1H NMR spectrum showed the resonances in Table I. On warming rearrangement occurred (L = PPh_3, $PMePh_2$, and 0.5dpp), and a second set of resonances were observed (see Table I). In the case L_2 = dpe the ^{13}C NMR spectrum of the dihydride adduct was also observed: vinyl dct carbons at δ 134.8, 134.6, 134.3, and 134.1 (s); quaternary dct carbons at δ 91.5 (s), 84.6 (d, $J = 2$), 79.4 (dt, $J = 2$ and 30, integration for two carbons).

Hydrido(dibenzo[*a*,*e*]cyclooctatetraene)bis(triphenylphosphine)iridium(I). Method A. To $[Ir(dct)(PPh_3)_2]BF_4$ (50 mg 0.05 mmol) in CH_2Cl_2/THF (3:5, 8 mL) at 0 °C was added $LiBHEt_3$ (0.1 mL of 1 M THF solution) slowly. The solution was stirred for 15 min, and the solvents were removed. The oily residue was dissolved in CH_2Cl_2 (5 mL) and filtered. $MeOH/H_2O$ (2:1, 5 mL) was added as an upper layer. Off-white crystals were deposited, washed with cold MeOH, and dried: yield 15 mg (30%); IR (CH_2Cl_2, cm^{-1}) 2132 (m), 1603 (m), 1481 (s), 870 (m), 821 (m).

Method B. To *cis,trans*-$[IrH_2(dct)(PPh_3)_2]BF_4$ (50 mg, 0.05 mmol) in CH_2Cl_2 (5 mL) was added potassium *tert*-butoxide (8 mg). After 10 min of stirring, $MeOH/H_2O$ (2:1, 10 mL) was added as an upper layer. Off-white crystals were deposited as in method A: yield 35 mg (70%). We prefer method B.

(Dibenzo[*a*,*e*]cyclooctatetraene)(1,2-bis(diphenylphosphino)ethane)iridium(I) Hexafluorophosphate. To $[Ir(dct)Cl]_2$ (100 mg, 0.23 mmol) and dpe (92 mg, 0.23 mmol) in CH_2Cl_2 (15 mL) was added $[Et_3O]PF_6$ (75 mg, 0.3 mmol). To the resulting red solution was added a layer of hexane (30 mL). Red crystals were formed, filtered, washed with hexane, and dried: yield 180 mg (84%); ^{13}C NMR δ 142.3 (s, quaternary dct carbons), 89.1 (t, $J = 5$, dct vinyls). Anal. Calcd for $C_{42}H_{36}IrP_3F_6$: C, 53.67; H, 3.86. Found: C, 53.62; H, 4.02.

(Dibenzo[*a*,*e*]cyclooctatetraene)(1,3-bis(diphenylphosphino)propane)iridium(I) Hexafluorophosphate. To $[Ir(dct)Cl]_2$ (100 mg, 0.23 mmol) and dpp (95 mg, 0.23 mmol) in CH_2Cl_2 (10 mL) was added $AgPF_6$ (58 mg, 0.23 mmol). After being stirred for 1 min, the red solution was filtered through Celite. The Celite was washed with CH_2Cl_2 (3 mL) and the combined filtrate reduced to 4 mL in vacuo. Et_2O/hexanes (1:1, 10 mL) was added as an upper layer, and the resulting red crystals were filtered, washed (hexane), and dried; yield 155 mg (71%).

(Dibenzo[*a*,*e*]cyclooctatetraene)tris(triethyl phosphite)iridium(I) Hexafluorophosphate. To $[Ir(dct)Cl]_2$ (50 mg) in EtOH (10 mL) was added $P(OEt)_3$ (0.25 mL) and the solution refluxed for 12 h. To the cooled solution was added saturated aqueous KPF_6 (1 mL), and the solvents were removed in vacuo. The CH_2Cl_2 (10 mL) extract was filtered and reduced to 3 mL in vacuo. Hexane (10 mL) was added, and the resulting white crystals were filtered, washed (hexane), and dried; yield 90 mg (75%). Anal. Calcd for $C_{34}H_{57}O_9P_4F_6Ir$: C, 39.27; H, 5.53. Found: C, 39.50; H, 5.60.

Chloro(dibenzo[*a*,*e*]cyclooctatetraene)rhodium(I). $[Rh(cod)Cl]_2$ (122 mg) in CH_2Cl_2 (5 mL) was treated with dct (100 mg) in CH_2Cl_2 (3 mL). Yellow crystals were deposited over several minutes. A layer of hexane (5 mL) was added to complete the precipitation. The resulting yellow crystals were filtered, washed (hexane), and dried; yield 100 mg (60%). This complex cannot be recrystallized, and it was used directly for subsequent preparations.

(Dibenzo[*a*,*e*]cyclooctatraene)bis(triphenylphosphine)rhodium(I) Hexafluorophosphate. To $[Rh(dct)Cl]_2$ (100 mg) and PPh_3 (153 mg) in CH_2Cl_2 (10 mL) was added $AgPF_6$ (74 mg). After 10 min of stirring the solution was filtered and the filtrate treated with hexane (20 mL) to give orange microcrystals, which were filtered, washed (hexane), and dried: yield 215 mg (76%). Anal. Calcd for $C_{52}H_{42}RhP_3F_6 \cdot CH_2Cl_2$: C, 59.96; H, 4.17. Found: C, 59.99; H, 4.32.

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Registry No. **2a**, 12112-67-3; **2b**, 84500-08-3; **3b** (L = PPh_3) BF_4, 84500-10-7; **3b** (L_2 = dpe) PF_6, 84500-15-2; **3b** (L_2 = dpp) PF_6, 84500-19-6; **3b** (L = $PMePh_2$)PF_6, 84500-23-2; **4b** (L = PPh_3) BF_4, 84500-12-9; **4b** (L_2 = dpe) PF_6, 84500-17-4; **4b** (L_2 = dpp) PF_6, 84581-01-1; **5b** (L = PPh_3) BF_4, 84580-15-4; **6b** (L = PPh_3), 84500-13-0; **7b** (L_2 = dpp) PF_6, 84500-21-0; **7b** (L = $PMePh_2$) PF_6, 84500-25-4; $[Ir(dct)(P\{OEt\}_3)_3]PF_6$, 84500-27-6; $[Rh(dct)Cl]_2$, 84500-28-7; $[Rh(dct)(PPh_3)_2]PF_6$, 84500-30-1; *cis,trans*-$[RhH_2(dct)(PPh_3)_2]PF_6$, 84500-32-3; *cis,trans*-$[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$, 82582-67-0; $[Rh(Cod)Cl]_2$, 12092-47-6.

X-ray Crystal Structure of the Mononuclear Tris(trimethyl phosphite)(maleic anhydride)cobalt(0) Complex

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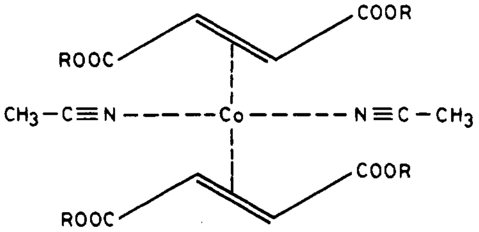
The crystal structure of a new mononuclear cobalt(0) complex with trimethyl phosphite and maleic anhydride (MA) ligands has been determined from X-ray diffractometer data. The crystals are monoclinic of space group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions $a = 9.517$ (4) Å, $b = 15.432$ (14) Å, $c = 16.915$ (8) Å, and $\beta = 113.17$ (6)°. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares techniques to $R = 0.063$ for 2726 independent reflections. The metal is linked to three P atoms of the trimethyl phosphite groups and to the CH═CH moiety of MA. The molecular structure of C_1 symmetry contains a pseudotetrahedrally coordinated Co atom with bond distances Co–P(mean) = 2.172 (2) Å, Co–C(olefinic)(mean) = 2.033 (7) Å, and Co–X = 1.898 Å and bond angles P–Co–P(mean) = 99.4 (4)° and P–Co–X 117.4° (X is the midpoint of the olefinic bond). The parameters and bonding of the (trimethyl phosphite)cobalt part of the complex are standard with a mean P–O distance of 1.594 (6) Å and indicates a certain degree of π bonding. The mean O–C bond length is 1.443 (12) Å; Co–P–O angles average to 117.1 (2)° and O–P–O to 100.6 (5)°. The bond lengths in the MA ring (with C_s symmetry) indicate strong π-electron delocalization, in accordance with the large decrease in ν(C═O) from 1780 and 1850 cm^{-1} in free MA to 1722 and 1787 cm^{-1} in the complex.

Introduction

Cobalt(0) complexes are catalytically active in hydrogenation, carbonylation, and oligo- and polymerization reactions. As part of the studies on the reactivity and structure of mononuclear d^9 metal complexes,[1-4] the intermediate I has been isolated and characterized.



I

Various mono- and polynuclear complexes are easily formed by partial or total displacement in I,[5] as shown in Figure 1. Of particular interest is the synthetic route to compounds II and III, as cobalt complexes with phosphitic ligands are known to be extremely active and selective hydrogenation catalysts.[6-8] In the presence of unsaturated ligands, these complexes allow for electron delocalization that may lead to interesting properties in terms of activity and selectivity. The elucidation of the structures of such complexes is therefore useful not only in establishing the nature of the coordination around cobalt(0) but also in gaining a better insight into the role of the metal in catalysis. Since only rather few examples of mononuclear d^9 complexes of cobalt have been prepared[4,9-13] and in view of the paucity of molecular structural data,[4,12] an X-ray study of tris(trimethyl phosphite)(maleic anhydride)cobalt(0) (COCA) was undertaken.

Experimental Section

Preparation. COCA was prepared by the total ligand displacement reaction involving addition of 5.0 g (40 mmol) of trimethyl phosphite and 1.0 g (10 mmol) of maleic anhydride to 4.85 g (10 mmol) of a toluene solution (50 mL) of bis(ethyl fumarate)bis(acetonitrile)cobalt(0) under continuous stirring until complete dissolution of the anhydride:

$$Co(CH_3CN)_2L_2 + 3P(OCH_3)_3 + MA \rightarrow [P(OCH_3)_3]_3CoMA + 2L + 2CH_3CN$$

L = ethyl fumarate; MA = maleic anhydride

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