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Ligand-Ligand Interactions in Arene Chromium Dicarbonyl-(Maleic anhydride) Complexes *

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A series of 10 maleic anhydride (MA) complexes of the general type $ArCr(CO)_2(MA)$ (Figure 1) has been prepared photochemically, starting from $ArCr(CO)_3$ compounds in which the nature of the π-bonded benzene ring (Ar) is modified by ring substituents. Comparison of IR and ¹H-NMR data in both $ArCr(CO)_3$ and $ArCr(CO)_2(MA)$ compounds indicates that π-bonded maleic anhydride is a more powerful electron-withdrawing ligand in these chromium complexes than carbon monoxide. Empirical Hammett correlations are used to demonstrate transmission of electronic effects through the metal atom. The different ligands coordinated at chromium in $ArCr(CO)_2(MA)$ complexes are involved in extensive ligand-ligand interaction.

Introduction

Electronic interactions between different ligands coordinated to the same metal atom are a well-documented phenomenon in coordination chemistry. It is known, for example, that the C≡O stretching frequencies in metal carbonyl complexes are very sensitive to variations in electronic structure of the complex caused by changes in ligand composition. It is more difficult, however, to demonstrate directly the ligand-ligand interactions between π-bonded olefins and π-bonded arene rings. The present study has been undertaken to investigate such interactions in complexes of the general type $ArCr(CO)_2(MA)$ (Figure 1). In these *bona-fide* octahedral complexes the central metal, chromium, is enclosed by three different neutral ligands: the π-bonded monoolefin, maleic anhydride (MA), the two carbon monoxide ligands, and the π-bonded arene ring (Ar), the nature of which can easily be modified by various ring substituents (S):

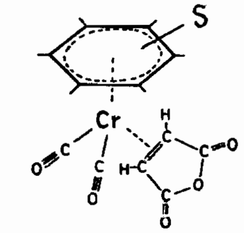

Figure 1. $ArCr(CO)_2(MA)$.

The choice of maleic anhydride as a π-olefinic ligand in these model compounds of the type $ArCr(CO)_2(MA)$ was prompted by two main reasons:

(a) The unsaturated cyclic anhydride, MA, has generally been found to be a good coordinating ligand if the metal is in a low oxidation state. Several maleic anhydride complexes have been prepared starting from either metal carbonyls or substituted metal carbonyl derivatives, e.g. $[M(CO)_2(MA)_3X]^-$ (M = Mo, W; X = Cl, Br),[2] CpM(CO)(NO)(MA) (M = Cr,[3] Mo[4]), $CpMn(CO)_2(MA)$,[1,5,6] $Fe(CO)_4(MA)$[7,8,9,10,11] $Fe(CO)_3(PPh_3)(MA)$,[8,10,11] $C_8H_{13}Co(CO)_2(MA)$[12] (C_8H_{13}= π-cyclo-octenyl) and $Ni(MA)_2$.[13] An additional group of olefin complexes is formally obtained by way of addition of maleic anhydride to coordinatively unsaturated d⁸ and d¹⁰ complexes, this group includes compounds such as $(Bu^t{-}N{\equiv}C)_2Ni(MA)$[14] and the triphenylphosphine complexes $(PPh_3)_2M(NO)(MA)$ (M = Co, Rh, Ir),[14a] $(PPh_3)_2IrCl(CO)(MA)$[15] and $(PPh_3)_2M(MA)$ (M = Pd,[16,17,18] Pt[17,19,20]); related complexes of

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(2) H.D. Murdoch, R. Henzi, and F. Calderazzo, *J. Organomet. Chem., 7*, 441 (1967).

(3) M. Herberhold and H. Alt, *J. Organometal. Chem., 42*, 407 (1972).

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(7) E. Weiss, K. Stark, J.E. Lancaster, and H.D. Murdoch, *Helv. Chim. Acta, 46*, 288 (1963).

(8) G.O. Schenck, E. Koerner von Gustorf, and M.-J. Jun, *Tetrahedron Letters*, 1059, Nr. 23 (1962).

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(10) E. Koerner von Gustorf, M.-J. Jun, H. Köller, and G.O. Schenck, « Industrial Uses of Large Radiation Sources », Vol. II. p. 73-85, International Atomic Energy Agency, Wien 1963.

(11) E. Koerner von Gustorf, H. Köller, M.-J. Jun, and G.O. Schenck, Atomstrahlung Med. Techn., 259 (1964).

(12) S. Otsuka and M. Rossi, *J. Chem. Soc. (A)*, 497 (1969).

(13) E. Weiss and K. Stark, *Z. Naturforsch., 206*, 490 (1965).

(14) S. Otsuka, T. Yoshida, and Y. Tatsuno, *Chem. Commun.*, 67 (1971).

(14a) G. La Monica, G. Navazio, P. Sandrini, and S. Cenini, *J. Organomet. Chem., 31*, 89 (1971).

(15) J.P. Collman and J.W. Kang, *J. Amer. Chem. Soc., 89*, 844 (1967).

(16) P. Fitton and J.E. McKeon, *Chem. Commun.*, 4 (1968).

(17) S. Takahashi and N. Hagihara, *Nippon Kagaku Zasshi, 88*, 1306 (1967); *C.A., 69*, 27514g (1968).

(18) S. Takahashi and N. Hagihara, *Yuki Gosei Kagaku Kyokay Shi, 28*, 360 (1970); *C.A., 72*, 132933c (1970).

(19) S. Cenini. R. Ugo, F. Bonati, and G. La Monica, *Inorg. Nucl. Chem. Letters, 3*, 191 (1967).

(20) S. Cenini, R. Ugo, and G. La Monica, *J. Chem. Soc. (A)*, 409 (1971).

the type $L_2Pd(MA)$ (e.g., L = $P(OMe)_3$,[21] $P(OPh)_3$;[21] L_2 = 1,2-bis(diphenylphosphino)ethane,[17] bipyridyl[21] and o-phenanthroline[21]) are also known.[22] In all maleic anhydride complexes the back-donation from the metal to the π-coordinated monoolefin appears to play an important part. It was of interest, therefore, to have two good "acceptor ligands", maleic anhydride and carbon monoxide, within the same molecule and to compare their electron-withdrawing capacity in $ArCr(CO)_2(MA)$ type complexes (Figure 1).

(b) Free maleic anhydride possesses characteristic IR absorptions, in particular the C=C stretching band (1596 cm^{-1} in nujol (solid))[24] and the C=O stretching bands of the dicarboxylic anhydride group (1869 and 1783 in nujol (solid)).[24] It could be reasonably expected that these absorptions would be detectable in the IR spectra of the π-olefin complexes, $ArCr(CO)_2(MA)$, and would reflect modifications of the olefin due to the complex formation. In a similar manner, the singlet due to the olefinic protons in the ^{1}H-NMR spectrum of maleic anhydride (τ = 2.67 in acetone-d_6) should also be observed as a characteristic signal in the ^{1}H-NMR spectra of the π-complexes. Thus, we hoped that these characteristic IR and ^{1}H-NMR absorptions could be used to monitor electronic interactions in the complexes, just as it is usual to discuss metal carbonyl complexes in terms of the C≡O stretching frequencies of the carbon monoxide ligands.

Experimental Section

General Remarks. All operations were carried out under an atmosphere of purified nitrogen. Solvents (THF, benzene, n-hexane) were anhydrous and N_2-saturated, and were distilled before use from deep blue solutions of benzophenone ketyl ($Ph_2CO + Na$). Silica gel (Kieselgel, 0.05-0.20 mm) was activated at 150-180°C under high vacuum for six hours and then allowed to cool under an atmosphere of dry nitrogen.

Photochemical reactions were carried out using a water-cooled medium pressure mercury arc (Hanovia S-200 W). The solutions were irradiated in Schlenk tubes (Jenaer Glas or Duran); the tubes served as light filters, absorbing light with wavelengths below 300 nm.

IR spectra were measured as KBr pellets on a Perkin-Elmer spectrometer Model 21; the ν(C≡O) and ν(C=O) region (4-6 μ) was also recorded for CH_2Cl_2 solutions using LiF optics. Calibration of the solution spectra was carried out using the atmospheric H_2O band at 1869.4 cm^{-1} (cf. ref. 1).

^{1}H-NMR spectra were measured on a Varian A 60 spectrometer in acetone-d_6 solution. The spectra were calibrated by a (external) TMS/$CHCl_3$ mixture (=436 Hz).

Preparation of Arene Chromium Tricarbonyls, $ArCr(CO)_3$. Direct thermal reaction of $Cr(CO)_6$ with a substituted benzene (Ar) in solution[25,26,27] has been used to prepare the starting complexes of the general type $ArCr(CO)_3$, according to

$$Cr(CO)_6 + Ar \rightarrow ArCr(CO)_3 + 3CO.$$

In the case of liquid arenes with boiling points above 120°C, a solution of $Cr(CO)_6$ in the aromatic solvent was refluxed until the calculated volume of CO had been evolved (Ar = *p*-xylene,[25] mesitylene,[25], anisole[25,26]); in the case of liquid arenes with boiling points below 100°C, the reaction was carried out in an autoclave at about 150°C (Ar = benzene,[26] fluorobenzene). Solid arenes were best converted into the desired $ArCr(CO)_3$ complex in a polyether solvent such as "diglyme" (b.p. ~165°C) [25,27] (Ar = hexamethylbenzene,[25] *p*-trimethylsilyl toluene,[27] methyl *p*-methyl benzoate,[27] *p*-(trimethylsilyl)-N,N-dimethyl aniline[27]). If a small amount of a more volatile ether (*p*-dioxane, dimethoxyethane) is added to the solution, $Cr(CO)_6$ is continuously washed back into the reaction vessel and does not solidify in the lower part of the reflux condenser.[27] The use of diglyme as a solvent may also be recommended for the reaction of liquid arenes with $Cr(CO)_6$ to give $ArCr(CO)_3$ type complexes.[25,27] Other high-boiling ethers such as di(*n*-butyl) ether can be used instead of diglyme (Ar = dimethyl terephthalate[28]).

The $ArCr(CO)_3$ complexes, prepared according to literature procedures,[25-28] were purified, if possible, by high vacuum sublimation at elevated temperatures: $ArCr(CO)_3$, Ar = hexamethylbenzene (100-120°C), mesitylene (80-100°), *p*-xylene (80-100°), benzene (70-90°), fluorobenzene (70-80°), anisole (70-80°), *p*-(trimethylsilyl)toluene (90-100°), methyl *p*-methyl benzoate (70-80°). The $ArCr(CO)_3$ complexes containing either *p*-(trimethylsilyl)-N,N-dimethyl aniline or dimethyl terephthalate were recrystallised from *n*-hexane/THF mixtures.

Preparation of Arene Chromium Dicarbonyl-(Maleic anhydride) Complexes, $ArCr(CO)_2(MA)$. Displacement of a single CO ligand from $ArCr(CO)_3$ complexes by maleic anhydride was carried out photochemically:[1]

$$ArCr(CO)_3 + MA \xrightarrow[\text{(THF)}]{h\nu} ArCr(CO)_2(MA) + CO$$

Two procedures were used to effect this photo-induced substitution (cf. ref. 29):

Method A: Direct irradiation of the starting com-

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[21] T. Ito, Y. Takahashi, and Y. Ishii, *Chem. Commun.*, 629 (1972).

[22] Transition metal complexes of maleic anhydride are, in general, mononuclear, the olefin being cordinated to one metal atom. A binuclear complex, $Fe_2(CO)_6L(MA)$ (L = 3,6-diphenylpyridazine), containing a bridging MA ligand has recently been described.[23]

[23] H.A. Patel and A.J. Carty, M. Mathew, and G.J. Palenik, *J. Chem. Soc., Chem. Commun.*, 810 (1972).

[24] P. Mirone and P. Chiorboli, *Spectrochim. Acta*, *18*, 1425 (1962).

[25] B. Nicholls and M.C. Whiting, *Proc. Chem. Soc.*, 152 (1958); *J. Chem. Soc.*, 551 (1959).

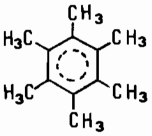
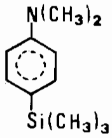
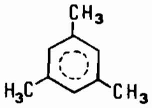
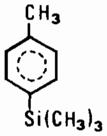
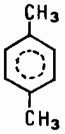
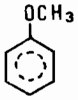
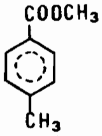
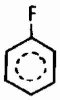
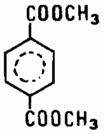
[26] E.O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J.P. Mortensen, and W. Semmlinger, *Chem. Ber.*, *91*, 2763 (1958).

[27] H.P. Fritz and C.G. Kreiter, *J. Organomet. Chem.*, 7, 427 (1967).

[28] W. Strohmeier and P. Hartmann, *Z. Naturforsch.*, *18b*, 506 (1963).

[29] W. Strohmeier, *Angew. Chem.*, 76, 873 (1964); *Angew. Chem.*, Int. Ed. Engl., 3, 730 (1964).

Table I. Preparation and analytical characterisation of arene chromium dicarbonyl-(maleic anhydride) complexes.

No	Complex $ArCr(CO)_2(MA)$ Ar =	Method of Preparation[a] (Yield)	Colour	Decomposition Temperature (°C)[b]	Analyses % Cr Calcd.	% Cr Found	% C Calcd.	% C Found	% H Calcd.	% H Found
1		A (12.8%) B (20.1%)	red-orange	218-220	14.12	14.24	58.69	58.53	5.47	5.71
2		B (9%)	red-brown	~175	13.02	12.67	51.12	51.32	5.30	5.14[c]
3		A (18.0%) B (29.8%)	red	180-182	15.94	16.01	55.22	55.06	4.33	4.30
4		B (50%)	red	168-170	14.04	14.09	51.88	51.84	4.90	4.95
5		B (17.3%)	red	167-169	16.66	16.71	53.85	53.53	3.87	4.02
6		B (20.3%)	red	154-156	16.55	16.56	49.69	49.58	3.21	3.50
7		A (9.2%)	red	189-192	18.30	18.42	50.71	50.71	2.84	2.83
8		B (51.3%)	red-brown	137-139	14.60	14.44	50.57	50.70	3.40	3.42
9		B (23%)	red-orange	144-146	17.21	17.11	47.69	47.50	2.34	2.49
10		B (44%)	brown	~160	12.99	12.60	48.01	47.40	3.02	3.02

[a] *A*: direct irradiation of $ArCr(CO)_3$+MA; *B*: Two-step reaction *via* intermediate THF complexes. [b] The decomposition temperature (in a sealed tube under N_2) depends on the rate of heating the sample; the temperatures indicated should be considered as approximate. [c] %N: Calcd. 3.51, Found 3.99%.

plex, $ArCr(CO)_3$, in the presence of excess maleic anhydride in tetrahydrofuran (THF) solution;

Method B: Irradiation of $ArCr(CO)_3$ in THF solution and subsequent displacement of coordinated THF by maleic anhydride in a dark reaction.

In both cases the primary excitation of $ArCr(CO)_3$ results in expulsion of a single CO ligand, and the free coordination position thus formed is then occupied either by the donor solvent THF (Methods A and B) or directly by the olefin, maleic anhydride (Method A). In the two-step procedure (B), complexes of the type $ArCr(CO)_2(THF)$ appear to be predominantly formed upon irradiating $ArCr(CO)_3$ in THF. The quality of the solvent THF (e.g. rigorous exclusion of oxygen and water) is essential for a successful application of method B. The yields of $ArCr(CO)_2(MA)$ complex are generally in the 10-50 per cent region and are higher for the indirect method (B).[1]

Table I presents properties and analytical data for the maleic anhydride complexes; the compounds are arranged according to the $\nu(C\equiv O)$ frequencies of the carbonyl ligands (cf. Table II). The procedures (A and B) used for the preparation of complexes *1-10* were essentially the same; two characteristic examples are given below:

Mesitylene Chromium Dicarbonyl-(Maleic anhydride) (*3*): *Method A*: 0.256 g (1 mmole) of mesitylene chromium tricarbonyl and 0.49 g (5 mmoles) of freshly sublimed maleic anhydride were dissolved in ca 100 ml of dry, N_2-saturated THF and irradiated with magnetic stirring at room temperature. After 1/2 hr the cloudy red solution was filtered through a G3 sintered glass disk covered with filter flock. The resulting clear red solution was further irradiated with intermittant filtration until gas evolution ceased (ca 5 hrs). Final filtration and removal of solvent left a deep red solid which was chromatographed on activated silica gel. Elution with benzene/THF (4:1) gave a yellow and a red band. The first (yellow) zone contained mesitylene chromium tricarbonyl (0.119 g, 46%, recovered). The second (red) zone left, after removal of solvent, 60 mg of (3) (18 per cent). Recrystallisation from CH_2Cl_2/pentane gave deep red needles of (3), dec. ~180-182°.

(Methyl p*-methyl benzoate)-Chromium Dicarbonyl-(Maleic Anhydride)* (*8*). *Method B*: 0.286 g (1 mmole) of (methyl *p*-methyl benzoate)-chromium tricarbonyl were dissolved in 100 ml of dry, N_2-saturated THF and irradiated at room temperature until gas evolution ceased (ca 6 hrs). Then 0.49 g (5 mmoles) of freshly sublimed maleic anhydride were added to the orange-red solution; the clear solution was then stirred for 2 hrs. Removal of solvent from the resulting bright red-brown solution gave a dark red solid which was chromatographed on activated silica gel. Elution with benzene separated unreacted starting material; further elution with increasing amounts of THF gave a red zone. After collection and removal of solvent, 183 mg of crystalline (8) (51.3%) were obtained. The product was recrystallised twice from either CH_2Cl_2/*n*-hexane or THF/*n*-hexane to give deep red crystals, which decomposed at 137-139° in a sealed tube (under N_2).

Results and Discussion

Photo-induced substitution of a single CO ligand by maleic anhydride in arene chromium tricarbonyls has been found to be a good method to combine a π-bonded six-membered ring (Ar) with a π-bonded olefin (MA) *via* a common $Cr(CO)_2$ link.[1] Both relatively electron-rich arene rings (hexamethylbenzene or anisole) and relatively electron-poor arene rings (fluorobenzene or dimethyl terephthalate) can be used in these model compounds:

$$ArCr(CO)_3+MA\xrightarrow[(THF)]{h\nu}ArCr(CO)_2(MA)+CO$$

The hexamethylbenzene complex (1) has been independently prepared by Angelici and Busetto.[30] The new maleic anhydride complexes (1-10) are red, crystalline solids which are stable in the solid state. The thermal stability is remarkably high; decomposition with liberation of MA occurs only in the 135-220°C region. As a general rule, the thermal stability decreases if the π-arene ring carries electron-withdrawing substituents (Table I). The π-olefin compounds, $ArCr(CO)_2(MA)$ (Figure 1), are considerably less soluble in organic solvents than the parent complexes, $ArCr(CO)_3$, and are not volatile under high vacuum (10^{-1}-10^{-2} Torr). While olefinic hydrocarbons such as ethylene, cyclopentene or cycloheptene are immediately displaced from their $ArCr(CO)_2$ (olefin) compounds by triphenylphosphine,[31] the maleic anhydride complex $(C_6Me_6)Cr(CO)_2(MA)$ (1) remains unchanged in the presence of tertiary phosphines (PPh_3, PBu_3^i) even in boiling benzene.[30]

IR Spectra. It is known that the electron density in arene chromium tricarbonyls may be varied considerably by both the number and the nature of ring substituents attached to the benzene ring. This is clearly reflected in the $C\equiv O$ stretching frequencies which are given in Table II. Increasing electron density on the metal will favour back-bonding to the carbonyl ligands, leading to increased population of the antibonding π* orbitals of the CO ligands and a concomitant lowering of the $\nu(C\equiv O)$ frequencies. In a simple valence bond picture, increasing metal-to-carbonyl back-bonding favours structure (b):

$$\underset{(a)}{\overline{M}-C\equiv O|}\;\longleftrightarrow\;\underset{(b)}{M=C=O\rangle}$$

Thus, a relatively low frequency of the two $C\equiv O$ stretching vibrations (of local symmetries A_1 and E) points to a relatively high electron density in the complex, as in $(C_6Me_6)Cr(CO)_3$. On the other hand, the increasing $\nu(C\equiv O)$ frequencies of the $ArCr(CO)_3$ compounds in Table II are a reliable indication that the charge density in the complex is stepwise lowered

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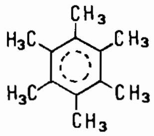
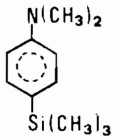
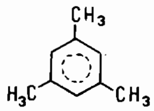
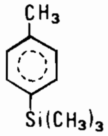
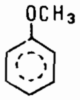
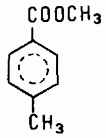
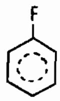
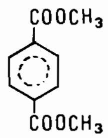
(30) R.J. Angelici and L. Busetto, *Inorg. Chem.*, *7*, 1935 (1968).
(31) W. Strohmeier and H. Hellmann, *Chem. Ber.*, *98*, 1598 (1965).

Table II. Characteristic IR data of $ArCr(CO)_3$ and $ArCr(CO)_2(MA)$ complexes.

No	Ar =	$ArCr(CO)_3$ [a]			$ArCr(CO)_2(MA)$ [a]					
		$\nu(C{\equiv}O)$ $[cm^{-1}]$ [b]		$k(C{\equiv}O)$ $[mdyn/Å]$ [c]	$\nu(C{\equiv}O)$ $[cm^{-1}]$ [b]		$k(C{\equiv}O)$ $[mdyn/Å]$ [c]	$\nu(C{=}O)$ $[cm^{-1}]$ [d]		$\Delta\nu(C{=}O)$ [e] $(cm^{-1}]$
1		1948	1861	14.43	1951	1888	14.88	1800	1738	52
2		1952	1862	14.46	1953	1891	14.92	1800	1733	52
3		1962	1878	14.68	1962	1902	15.08	1804	1739	48
4		1964	1883	14.75	1964	1906	15.12	1806	1741	46
5		1966	1880	14.72	1965	1907	15.14	1805	1739	47
6		1969	1884	14.77	1970	1912	15.22	1805	1739	47
7		1973	1890	14.86	1974	1916	15.29	1806	1739	46
8		1980	1906	15.06	1978	1925	15.38	1810	1743	42
9		1981	1901	15.01	1980	1927	15.41	1809	1742	43
10		1995	1928	15.36	1992	1948	15.66	1816	1734	36

[a] All values refer to CH_2Cl_2 solution; error limit $\Delta\nu \pm 2$ cm^{-1}. [b] $C{\equiv}O$ Stretching frequencies of the carbonyl ligands. [c] Cotton-Kraihanzel force constant[32], calculated from the $\nu(C{\equiv}O)$ frequencies in CH_2Cl_2. [d] $C{=}O$ Stretching frequencies of π-bonded MA; $\nu(C{=}O)$ frequencies of free MA are 1852 and 1782 cm^{-1}, in CH_2Cl_2. [e] Frequency decrease of the higher-frequency $\nu(C{=}O)$ absorption of MA due to π-complex formation.

Table III. $C\equiv O$ Stretching frequencies of hexamethylbenzene complexes of the type $(C_6Me_6)Cr(CO)_2L$.

	$\nu(C\equiv O)[cm^{-1}]$		Measured in	Ref.
L = Quinoline	1848	1793	C_6H_6	35; cf. 31, 36
2,3-Diaza-bicyclo[2.2.1]heptene-2	1860	1798	C_6H_6	35
Triphenylphosphine	1865	1805	C_6H_6	35; cf. 31, 36
Benzonitrile	1869	1811	C_6H_6	35; cf. 31, 36
Cyclopentene	1883	1835	C_6H_6	31
Ethylene	1890	1835	C_6H_6	31
Norborn-5-ene-2,3-dicarboxylic anhydride	1902	1838	C_6H_6	30
Molecular nitrogen	1897	1848	C_6H_6	35; cf. 37
Phenylacetylene	1908	1838	C_6H_6	31
Diphenylacetylene	1912	1835	C_6H_6	31
Diethyl acetylene dicarboxylate	1934	1866	C_6H_6	31
Maleic acid	1924	1877	KBr	30
Fumaric acid	1933	1861	KBr	30
Citraconic anhydride	1959	1893	$CHCl_3$	30
Maleic anhydride	1967	1906	$CHCl_3$	30
	1951	1888	CH_2Cl_2	*a*

[a] Present work

in this order and the chromium-to-carbonyl back-bonding is reduced.

A very similar influence of the π-bonded arene ring on the $C\equiv O$ stretching frequencies is observed in the $ArCr(CO)_2(MA)$ series (Table II). Again, electron-withdrawing substituents at the benzene ring lower the electron density in the complex and therefore result in a reduction of the metal-to-carbonyl back-bonding in the order 1 to 10. It is interesting to note that the highest $\nu(C\equiv O)$ frequency (local symmetry A_1) does not show a significant shift upon substitution of maleic anhydride for carbon monoxide on going from $ArCr(CO)_3$ to $ArCr(CO)_2(MA)$. Somewhat larger shifts were observed for the lower-frequency bands but as they belong to different symmetry species (a doubly degenerate E for $ArCr(CO)_3$ and B for $ArCr(CO)_2(MA)$), no comparison can be made. The symmetry problem has been eliminated by calculating stretching force constants, $k(C\equiv O)$, according to the Cotton-Kraihanzel approximation[32] for the two cases of local symmetry C_{3v} ($ArCr(CO)_3$) and C_{2v} ($ArCr(CO)_2(MA)$). Although the simplified Cotton-Kraihanzel approach has been much criticised[33,34] and the $k(C\equiv O)$ values obtained by this method may indeed differ considerably from the "true" $C\equiv O$ force constants, we nevertheless feel that these $k(C\equiv O)$ values show at least the correct trends of metal-to-carbonyl back-bonding inherent in the two series of complexes, $ArCr(CO)_3$ and $ArCr(CO)_2(MA)$. As expected, the stretching force constants, $k(C\equiv O)$, become larger as the donating properties of the six-membered ring decrease and its acceptor properties increase (Table II).

Photo-induced substitution of carbon monoxide by maleic anhydride in $ArCr(CO)_3$ leads to a significant increase of the $k(C\equiv O)$ value by 0.3-0.5 [mdyn/Å], indicating that the remaining two CO ligands in $ArCr(CO)_2(MA)$ compounds are less involved in Cr→CO back-bonding than in the parent complex. The new ligand, MA, is apparently able to withdraw more charge from the occupied chromium d-orbitals of appropriate symmetry than the CO ligand which is displaced. Thus, maleic anhydride is a more powerful electron-withdrawing ligand in these complexes than carbon monoxide.[1,2]

Table III presents some hexamethylbenzene complexes of the general type $(C_5Me_6)Cr(CO)_2L$ for which $C\equiv O$ stretching frequencies have been reported. It becomes quite clear from this list that the donor-acceptor properties of the ligand L affect the $\nu(C\equiv O)$ frequencies. Increasing $\nu(C\equiv O)$ values indicate that the electron-withdrawing properties of the ligand L increase; this can be due either to a reduced L→Cr σ-bond or to an increased Cr→L π-bond, or to a combination of these two effects. Although the $\nu(C\equiv O)$ frequencies given in Table III cannot be exactly related to each other because of the differing conditions of measurement (i.e. different solvents), the high electron-withdrawing capacity of maleic anhydride is evident. It appears that, among all olefins and acetylenes investigated so far, maleic anhydride causes a particularly large polarisation of the electric charge towards the unsaturated ligand L.

Participation of the ligand MA in metal-to-ligand back-bonding may be deduced from the $C=O$ stretching absorptions of the dicarboxylic anhydride group which are lower in the $ArCr(CO)_2(MA)$ complexes than in free maleic anhydride (1852 and 1782 cm^{-1}, in CH_2Cl_2).[38] This lowering in frequency suggests that the dicarboxylic anhydride moiety receives a good deal of the charge which is transferred from the metal to the electron-withdrawing olefin, MA. The decrease is larger when electron-donating substituents at the π-benzene ring raise the electron density in the $ArCr(CO)_2(MA)$ complex (Table II), and there is a nearly linear relationship between the stretching

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(32) F.A. Cotton and C.S. Kraihanzel, *J. Amer. Chem. Soc. 84*, 4432 (1962).

(33) L.M. Bower and M.H.B. Stiddard, *Inorg. Chim. Acta, 1*, 231 (1967).

(34) L.H. Jones, *Inorg. Chem.*, 6, 1269 (1967); *Inorg. Chem.*, 7, 1681 (1968); *cf. F.A. Cotton, Inorg. Chem.*, 7, 1683 (1968).

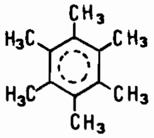
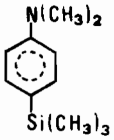
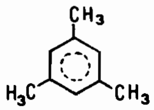
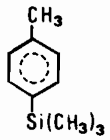
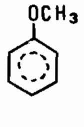
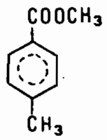
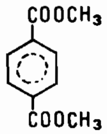
(35) M. Herberhold and K. Leonhard, unpublished results.

(36) W. Strohmeier and H. Hellmann, *Chem. Ber.*, *97*, 1877 (1964).

(37) D. Sellmann and G. Maisel, *Z. Naturforsch.*, *27b*, 465 (1972).

(38) The high-frequency $C=O$ stretching band belongs to the in-phase vibration (A_1), the low-frequency band to the out-of-plane vibration (B_1).[24] In free MA the low-frequency absorption is much more intense and is found to be split, the intensity ratio of the bands depending on the nature of the solvent. However, the $ArCr(CO)_2(MA)$ complexes (in CH_2Cl_2 solution) generally show two $\nu(C=O)$ bands of comparable intensity.

Table IV. Characteristic ^{1}H-NMR data of ArCr(CO)$_3$ and ArCr(CO)$_2$(MA) complexes.

		ArCr(CO)$_3$ [a]		ArCr(CO)$_2$(MA) [a]			
No	Ar =	τ(Ar)	τ(CH$_3$)	τ(Ar)	τ(CH$_3$)	τ(olefin)	Δτ(olefin) [b]
1		—	7.75	—	7.71	7.10	4.43
2		4.55 [c]	9.73(Si) 7.05(N)	4.28 [c]	9.60(Si) 6.86(N)	6.34	3.67
3		4.79	7.81	4.11	7.76	6.47	3.80
4		4.45 [c]	9.73(Si) 7.80	4.01 [c]	9.52(Si) 7.69	6.09	3.42
5		4.48	7.89	4.08	7.73	6.29	3.62
6		~4.47 [d]	6.22(O)	~3.97 [d]	6.00(O)	6.10	3.43
7		4.39	—	3.85	—	5.86	3.19
8		4.06 [c]	6.13(COO) 7.69	3.63 [c]	5.98(COO) 7.62	6.04	3.37
9		~4.21 [d]	—	~3.68 [d]	—	5.86	3.19
10		3.71	6.08(COO)	3.36	5.94(COO)	5.94	3.27

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[a] All values refer to acetone-d$_6$ solution with TMS as an internal reference; error limit Δτ ± 0.02 ppm. [b] Shift of the MA proton singlet due to π-complexation; τ(olefin) of free MA is 2,67. [c] Centre of gravity of the A,A′,B,B′ system (cf. ref. 27). [d] Centre of gravity of the multiplet.

Table V. ^{1}H-NMR Data of π-complexes containing maleic anhydride.

Complex	Solvent	τ(olefin) [a]	Δτ(olefin) [b]	Ref.
$CpCr(CO)(NO)(MA)$	Acetone-d_6	5.32; 6.16 (AB;$J_{H,H}$ 4.6 Hz)	3.07	3
$CpMo(CO)(NO)(MA)$	Acetone-d_6	5.50; 6.15 (AB;$J_{H,H}$ 5.0 Hz)	3.16	4
$C_6H_6Cr(CO)_2(MA)$	Acetone-d_6	5.86 (s)	3.19	*c*
$ArCr(CO)_2(MA)$	Acetone-d_6	5.86 - 7.10 (s)	3.19 - 4.43	*c*
$[Mo(CO)_2(MA)_3Cl]^-$	Acetone-d_6	5.78 (AB;$J_{H,H}$ 5 Hz)	3.13	2
$CpMn(CO)_2(MA)$	Acetone-d_6	5.59 (s)	2.92	5, 6
$Fe(CO)_4MA$	Acetone-d_6	5.63 (s)	2.98	7
	Acetone-d_6	5.63 (s)	3.01	8
	$CDCl_3$	5.93 (s)	3.06	8
$(Bu^t{-}N{\equiv}C)_2Ni(MA)$	Benzene	6.19 (s)		14
$(PPh_3)_2Rh(NO)(MA)$	$CDCl_3$	5.98 (d)	~3.08	14a
$(PPh_3)_2Ir(NO)(MA)$	C_6D_6	6.62 (d) ($J_{P,H} \simeq 7$ Hz) [d]		14a
$(PPh_3)_2Pd(MA)$	$CDCl_3$	6.0 (d) ($J_{P,H}$ 5.5 Hz) [d]		16
	C_6D_6	5.96; 6.11 (d) ($J=7.0$ Hz)		17
$(PPh_3)_2Pt(MA)$	$CDCl_3$	6.69 (d) ($J_{P,H}$ 6.5 Hz) [d,e]	3.79	20

[a] s = singlet, d = doublet, AB = AB system. The ^{1}H-^{1}H spin coupling constant of the olefinic protons in free MA has been determined from ^{13}C-NMR spectra to be about 5.6-6.2 Hz, depending on the solvent[43,44]. [b] Δτ(olefin) indicates the upfield shift of the MA protons due to π-complexation, referring to free MA in the same solvent. [c] Present work. [d] Only one phosphorus atom (the one in *trans* position) is found to couple with the olefinic proton. [e] Two satellite doublets are observed due to ^{195}Pt-^{1}H spin-spin coupling ($J_{Pt,H}$ = 56.5 Hz).

force constants $k(C{\equiv}O)$ of the two chromium-carbonyl ligands and the frequency decrease of the higher $C{=}O$ stretching absorption in the anhydride group (see below). However, π-complexation of MA leads only to relatively small frequency shifts of the $\nu(C{\equiv}O)$ anhydride vibrations, indicating that the dicarboxylic anhydride group is a considerably less sensitive probe for the electron-withdrawing capacity of MA than the $\nu(C{\equiv}O)$ vibrations of the carbonyl ligands which are directly bound to metal. Nevertheless, the lowering of the $C{=}O$ stretching frequencies clearly points to the importance of the $Cr{\rightarrow}MA$ back-bonding (cf. ref. 20).

IR evidence for a metal-olefin π-bond is provided by the absence of the $C{=}C$ stretching absorption which is observed at ca 1590 cm^{-1} in free maleic anhydride.[39] It is to be expected that the $C{=}C$ stretching frequency of MA is lowered as a result of π-complex formation, as has been reported for numerous π-olefin complexes. In general, the decrease of the $\nu(C{=}C)$ frequency is considered to be in the 100-150 cm^{-1} range,[40] although the assignment of this absorption is the matter of renewed discussion.[41] We have been unable to detect a band of this kind in the 1600-1400 cm^{-1} region of our IR spectra. Careful comparison of KBr spectra of both $ArCr(CO)_3$ and $ArCr(CO)_2(MA)$ complexes leads to the conclusion that the lowering of the $\nu(C{=}C)$ frequency of MA in these complexes must be >200 cm^{-1}, but we hesitate to assign a weak new band in the 1350-1400 cm^{-1} area to this $\nu(C{=}C)$ vibration especially as the IR spectra of our $ArCr(CO)_2(MA)$ complexes contain many absorptions due to the π-bonded arene ring. It is interesting to remark in this connection that, although many complexes containing maleic anhydride are known, in no case has a $C{=}C$ stretching frequency of the π-bonded olefin been reported.

^{1}H-NMR Spectra. The singlet due to the olefinic protons of free maleic anhydride (2.67 τ in acetone-d_5) is shifted considerably upfield by about 3.2-4.4 ppm in the $ArCr(CO)_2(MA)$ complexes (Table IV). A large upfield shift of the olefinic proton signal is characteristic of π-complexes in which the metal-to-olefin back-bonding plays an important part;[42] indeed, such a shift is commonly found in coordination compounds containing π-bonded maleic anhydride, both in substituted metal carbonyl derivatives and in bis(*tert.* phosphine) complexes of the noble metals. Table V gives a collection of literature data. This upfield shift of the olefinic protons is considered to be the most reliable evidence that π-complexation of MA through the $C{=}C$ double bond has taken place. Diamagnetic shielding by the metal appears to have a considerable effect on the magnitude of the shift; the particularly large upfield shift in the case of MA complexes might also indicate that the olefinic hydrogen atoms are twisted out of the ring plane of maleic anhydride to become bent away from the metal. While the olefinic protons in free MA lie directly in the deshielding cone of the carbonyl groups, the hydrogen atoms in π-coordinated MA may no longer be

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(39) The following frequencies have been given:[24] a) solid: 1596 cm^{-1} (nujol), 1595 cm^{-1} (film); b) liquid: 1590 cm^{-1}, Raman 1590(p) cm^{-1}.

(40) M. Herberhold, in « Metal π-Complexes », Vol. II., « Complexes with Mono-Olefinic Ligands », Part 2, Specific Aspects (Chapter VI. 1). Elsevier Publishing Company, Amsterdam, in press.

(41) J. Hiraishi, *Spectrochim. Acta, 25A,* 749 (1969); J. Hiraishi, D. Finseth, and F.A. Miller, *Spectrochim. Acta, 25A,* 1637 (1969).

(42) Ref. 40, Chapter VI. 3.

(43) H.M. Hutton and T. Schaefer, *J. Phys. Chem.*, 68, 1602 (1964).

(44) C. Ganter, L.G. Newman, and J.D. Roberts, *Tetrahedron, Suppl. 8, Part II,* 507 (1966).

coplanar with the MA ring framework due to partial rehybridisation of the olefinic carbon atoms towards sp^3.

It should be pointed out that a singlet is always observed for the olefinic protons in $ArCr(CO)_2(MA)$ complexes, thus requiring at least local C_2 symmetry at the $Cr(CO)_2(MA)$ group. This also indicates that the C=C double bond in $ArCr(CO)_2(MA)$ is symmetrically bound to the metal. By way of contrast, the equivalence of the olefinic MA protons is lost in coordination compounds such as $[Mo(CO)_2(MA)_3Cl]^-$,[2] $CpCr(CO)(NO)(MA)$[3] or $CpMo(CO)(NO)(MA)$,[4] and an AB type spectrum is observed for the ligand MA in the ^{1}H-NMR spectra.

Table IV also shows the chemical shifts of the arene protons for both $ArCr(CO)_3$ and $ArCr(CO)_2(MA)$ complexes. In all cases the ^{1}H-NMR signal of the aromatic protons moves *downfield* upon replacement of a CO ligand in $ArCr(CO)_3$ by the electron-withdrawing olefin maleic anhydride. This shift is most likely a result of decreased electron density on the metal and concomitant reduction of the shielding influence of the metal on the arene protons. Thus, the ^{1}H-NMR data confirm the conclusion drawn from the stretching force constants k(C≡O) that π-bonded maleic anhydride is a more powerful electron-withdrawing ligand in these chromium complexes than carbon monoxide. It is interesting to note that even the signals of the ring substituents (CH_3, CH_3O, $(CH_3)_3Si$, $(CH_3)_2N$) always move slightly to lower fields on going from $ArCr(CO)_3$ to $ArCr(CO)_2(MA)$ complexes (Table IV). A considerable influence of the electron density at the metal upon both the stretching force constant k(C≡O) and the chemical shift of the aromatic ring protons has also been observed for a series of π-cyclopentadienyl complexes of the type $CpMn(CO)_2L$ (L = five-membered cycloolefin[6] or unsaturated nitrile[45,46]) and for various other π-cyclopentadienyl complexes.[47] Shifts of the cyclopentadienyl ring proton signal to lower fields were only observed in the $CpMn(CO)_2L$ series if a CO ligand in $CpMn(CO)_3$ was replaced by an electron-withdrawing group stronger than carbon monoxide.[6,46]

Ligand-Ligand Interactions. The fact that the C≡O stretching frequencies in both $ArCr(CO)_3$ (cf. refs. 48, 49) and $ArCr(CO)_2(MA)$ are sensitive to the nature of the substituents at the π-bonded arene ring (Table II) is evidence that electronic effects are transmitted to the CO ligands through the central chromium atom. Figure 2 presents a plot of the Hammett ring substituent constants σ_{para}[50] *versus* the Cotton-Kraihanzel force constants k(C≡O) (Table II). It appears that an approximately linear correlation exists between the sum of the σ_p values for each individual ring substituent, $\Sigma\sigma_p$, and the stretching force constants, k(C≡O), as was also observed by Klopman and Noack.[49] This is an empirical relationship: the corresponding constants σ_m (characteristic of substituents in a *meta* position) did not show a linear relation with the k(C≡O) values, indicating that the influence of the ring substituents is based upon both inductive and resonance effects. No correlation has been observed when the stretching force constants k(C≡O) were plotted *versus* the Taft constants (σ_R and σ_I, respectively)[51] which separately describe resonance and inductive effects. Direct proportionality between k(C≡O) and ring substituent parameters in $ArCr(CO)_3$ and $ArCr(CO)_2(MA)$ compounds is only obtained if both resonance and inductive substituent constants, $(\sigma_R+\sigma_I)$, are taken into account. Similar correlations between Hammett substituent constants, σ, and C≡O stretching frequencies were also observed in other transition metal carbonyl complexes, e.g. in ring-substituted cyclopentadienyl manganese tricarbonyls,[52] $(X\text{-}C_5H_4)Mn(CO)_3$, in (methoxy-phenyl-carbene)-chromium pentacarbonyls,[53,54] $Cr(CO)_5\text{-}[C(OMe)C_6H_4\text{-}X]$, and (amino-phenyl-carbene)-chromium pentacarbonyls,[55] $Cr(CO)_5[C(NH_2)C_6H_4\text{-}X]$, in (1-phenyl-butadiene-1,3)-iron tricarbonyls,[56] $Fe(CO)_3\text{-}[CH_2{=}CHCH{=}CH\text{-}C_6H_4\text{-}X]$, and in cyclopentadienyl iron dicarbonyl σ-aryl complexes,[57] $CpFe(CO)_2\text{-}(C_6H_4\text{-}X)$.

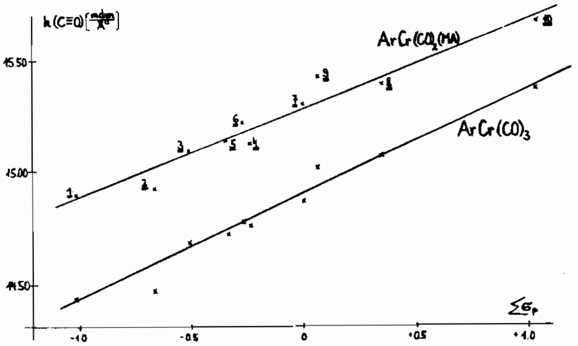

Figure 2. Relationship between the stretching force constants, k(C≡O), and the sum of the Hammett parameters, $\Sigma\sigma_p$, of the ring substituents, in $ArCr(CO)_3$ and $ArCr(CO)_2(MA)$ complexes. (Ar = six-membered arene ring, Ma = maleic anhydride; cf. Table II for the k(C≡O) values and the numbering system).

Ligand-ligand interactions were also found to exist between the π-bonded olefin MA and both the π-arene ring and the carbonyl groups. There is no correlation to be observed between the ^{1}H-NMR chemical shifts of π-bonded anhydride, τ(olefin) or Δτ(olefin), respectively, and either the stretching force constants, k(C≡O), or the Hammett constants, $\Sigma\sigma_p$.

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(45) M. Herberhold and H. Brabetz, *Chem. Ber.*, *103*, 3909 (1970).
(46) M. Herberhold and H. Brabetz, *Angew.*, *81*, 921 (1969); *Angew. Chem. Int. Ed. Engl.*, *8*, 902 (1969).
(47) R.B. King, *Inorg. Chim. Acta*, *2*, 454 (1968).
(48) R.D. Fischer, *Chem. Ber.*, *93*, 165 (1960).
(49) G. Klopman and K. Noack, *Inorg. Chem.*, *7*, 579 (1968).
(50) The Hammett constants, σ_p, given by Jaffé have been used: H.H. Jaffé, *Chem. Rev.*, *53*, 191-261 (1953), as quoted in H.A. Staab, « Einführung in die Theoretische Organische Chemie », 4. Auflage, Verlag Chemie, Weinheim, 1964, p. 584.
(51) R.W. Taft, jr., *J. Amer. Chem. Soc.*, *79*, 1045 (1957). R.W. Taft, jr., and H.D. Evans, *J. Chem. Phys.*, *27*, 1427 (1957). R.W. Taft, jr. and I.C. Lewis, *J. Amer. Chem. Soc.*, *80*, 2436 (1958).
(52) A.N. Nesmeyanov, K.N. Anisimov, B.V. Lokshin, N.E. Kolobova, and Yu.-V Makarov, *Dokl. Akad. Nauk SSSR*, *176*, 1082 (1967); *Proc. Acad. Sci. USSR, Chem. Sect.*, *176*, 908 (1976).
(53) E.O. Fischer, H.J. Kollmeier, C.G. Kreiter, J. Müller, and R.D. Fischer, *J. Organomet. Chem.*, *22*, C39 (1970).
(54) E.O. Fischer, C.G. Kreiter, H.J. Kollmeier, J. Müller, and R.D. Fischer, *J. Organomet. Chem.*, *28*, 237 (1971).
(55) E.O. Fischer and H.J. Kollmeier, *Chem. Ber.*, *104*, 1339 (1971).
(56) J.M. Landesberg and L. Katz, *J. Organomet. Chem.*, *35*, 327 (1972).
(57) E.S. Bolton, G.R. Knox, and C.G. Robertson, *Chem. Commun.*, 664 (1969).

However, a linear relationship may again be detected if the higher C=O stretching frequency (A_1) of the anhydride group, ν(C=O), is plotted *versus* either k(C≡O) or $\Sigma\sigma_p$. This higher ν(C=O) frequency (1852 cm^{-1} in free MA, in CH_2Cl_2) is lowered as a result of π-complexation at the olefinic C=C double bond, the frequency decrease, Δν(C=O), being larger in electron-rich $ArCr(CO)_2(MA)$ complexes (52 cm^{-1} in 1) than in electron-poor complexes (36 cm^{-1} in 10). A plot of Δν(C=O) *versus* the stretching force constants, k(C≡O), is given in Figure 3. The relatively small differences between the Δν(C=O) values in the series 1 to 10 again point to the fact that the anhydride group is only an insensitive probe for metal-to-ligand charge transfer.

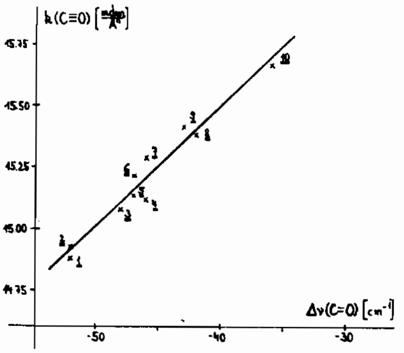

Figure 3. Relationship between the stretching force constant, k(C≡O), and the frequency decrease of the higher-frequency stretching vibration of the anhydride group, Δν (C=O), in $ArCr(CO)_2(MA)$ complexes (cf. Table II).

The linear correlations observed between the carbonyl stretching force constants, k(C≡O), the frequency decrease of the in-phase stretching vibration (A_1) of the anhydride group, Δν(C=O), and the Hammett constants of the arene substituents, $\Sigma\sigma_p$, indicate that all three kinds of ligands in $ArCr(CO)_2(MA)$ complexes participate in ligand-ligand interactions. If the electron density in the complex is changed by substituting one of the ligands, the neighbouring ligands are immediately adjusted to the new situation through the donor-acceptor metal-ligand bonding mechanism. The central metal appears to function as an electron bridge and to balance the donor-acceptor properties of the different ligand systems within the complex in order to minimize changes in the formal oxidation state of the metal.

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