Charge-transfer Interactions between Sulfur Dioxide and Group 8 Half-sandwich Complexes

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Mulliken-type charge-transfer complexes have been formed between basic half-sandwich compounds and SO_2 when $[M(\eta^5\text{-}C_5R_5)(CO)_2]$ (M = Rh or Ir; R_5 = Me_5, H_5 or H_4CF_3), $[Ir(\eta^5\text{-}C_5H_5)(CO)(C_2H_4)]$, and $[M(\eta^5\text{-}C_5H_5)(C_2H_4)_2]$ (M = Co, Rh or Ir) are isolated in SO_2-doped argon matrices at 20 K; the ν(CO) bands of the complexes are shifted to high frequency of those of the precursor molecules and prominent charge-transfer bands are observed; the same species have been detected when the compounds $[M(\eta^5\text{-}C_5Me_5)(CO)_2]$ (M = Rh or Ir) are embedded in polyethylene discs and treated with SO_2 at 213–298 K; the enthalpy of complexation of $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ with SO_2 is -13 ± 3 kJ mol^{-1}.

Kubas[1] has argued that sulfur dioxide is the most versatile ligand or complexing agent known, and has shown how its oxygen transfer reactions at organometallic centres may be used for catalytic formation of elemental sulfur. In one of the earliest examples of complexation, Cramer[2] showed that SO_2 reacts with $[Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2]$ to form $[Rh(\eta^5\text{-}C_5H_5)(C_2H_4)(SO_2\text{-}S)]$ at −80 °C. This substitution reaction was postulated to occur at exceptionally low temperature because the SO_2 could act initially as a Lewis acid towards the rhodium complex. No further examples of the Group 8 half-sandwich complexes have been discovered, probably because they are hard to control. We now report that SO_2 forms charge-transfer (c.t.) complexes, without substitution, with a variety of Group 8 half-sandwich compounds, and that such complexes can be characterised in low-temperature matrices and in polyethylene discs.

The IR spectrum of $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ isolated in a pure argon matrix at 20 K shows two ν(CO) bands at 2026 and 1959 cm^{-1}.[3] The UV/VIS spectrum shows no bands in the region $\lambda > 400$ nm. When the experiment is repeated with an argon matrix containing 1.2% SO_2 a prominent band is observed in the UV/VIS spectrum at 418 nm [Fig. 1(*a*)] and the IR spectrum shows two new ν(CO) bands to higher wavenumber of each of the bands of uncomplexed $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ [marked C in Fig. 2(*a*)]. The new bands have complex shapes with several shoulders. No 'free' CO is detected in the matrix. At lower SO_2 concentrations (0.6 and 0.3%) the absorbances of the UV/VIS band and the new IR bands [Fig. 1(*a*) (*ii*) and 2(*b*)] decrease relative to the unperturbed $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$, but the intensities of the four new IR bands are little changed relative to one another. The UV/VIS band shifts 5 nm to 413 nm in the matrix doped with 0.6% SO_2. Spectra have also been recorded in SO_2–Ar matrices for $[Rh(\eta^5\text{-}C_5Me_5)(CO)_2]$, $[M(\eta^5\text{-}C_5R_5)(CO)_2]$, (M = Rh or Ir; R_5 = H_5 or H_4CF_3),† and $[Ir(\eta^5\text{-}C_5H_5)(CO)(C_2H_4)]$. The IR spectra show the presence of several extra bands on addition of SO_2, which invariably lie to high frequency of those of the precursor in pure argon (Table 1).* The UV/VIS maxima vary with ligand

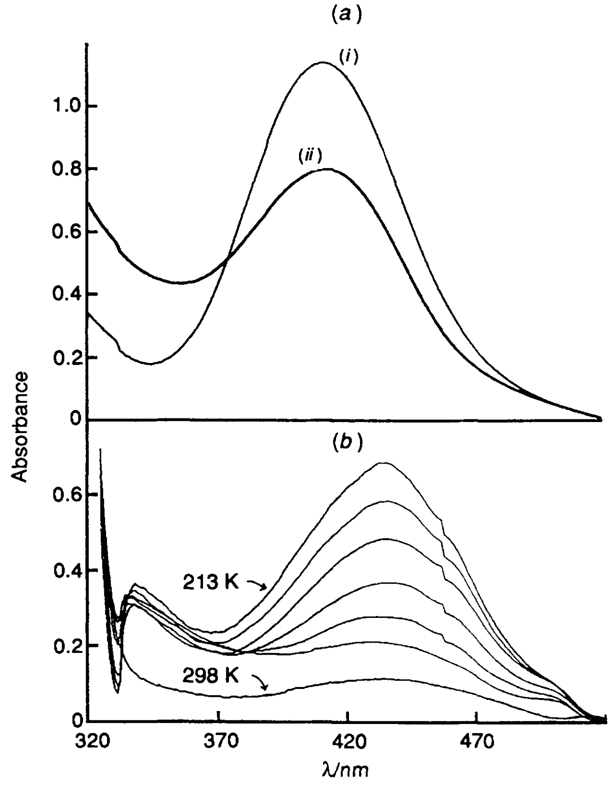

Fig. 1 The UV/VIS spectra for $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ (*a*) deposited in a cryogenic matrix (20 K) of argon with (*i*) 1.2 and (*ii*) 0.6% SO_2; (*b*) deposited in a low density polyethylene disc under 0.2 atm SO_2. The spectra show the growth of a band at 427 nm upon cooling the disc from 298 K to 213 K. The smaller band is assigned to the 'irreversible' product

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† $[Rh(\eta^5\text{-}C_5H_4CF_3)(CO)_2]$ was synthesised by treatment of $[Tl(\eta^5\text{-}C_5H_4CF_3)]^4$ with $[\{Rh(CO)_2Cl\}_2]$ in Et_2O. The iridium analogue was made by treating an Et_2O solution of $[\{IrL_2(CO)Cl\}_2]$ (L = cyclooctene) with CO followed by $[Tl(\eta^5\text{-}C_5H_4CF_3)]$. $^{13}C\text{-}\{^1H\}$ NMR data for $[M(\eta^5\text{-}C_5H_4CF_3)(CO)_2]$ in $CDCl_3$: M = Rh, δ 189.4 [d, *J*(RhC) 85, CO], 123.3 [q, *J*(FC) 268, CF_3], 100.6 [dq, *J*(FC) 39, *J*(RhC) 5, CCF_3], 89.7 [d, *J*(RhC) 4, CH], 86.9 (m, CH); M = Ir, δ 170.3 (s, CO), 122.8 [q, *J*(FC) 269, CF_3], 96.2 [q, *J*(FC) 40, CCF_3], 85.6 (s, CH), 83.8 [q, *J*(FC) 2 Hz, CH].

* The region from 1100 to 1400 cm^{-1} in the IR spectrum is dominated by the bands of SO_2; no product bands can be distinguished.

Table 1 Spectroscopic data for SO_2 charge-transfer complexes

	ν_{sym}/cm^{-1}		$\nu_{antisym}/cm^{-1}$		λ_{max}/nm
Matrix*	Ar	Ar–SO_2	Ar	Ar–SO_2	Ar–SO_2
$[Ir(\eta^5-C_5Me_5)(CO)_2]$	2026	2034	1959	1981, 1966	418
$[Ir(\eta^5-C_5H_5)(CO)_2]$	2044	2050, 2048	1977	1991, 1982	405
$[Ir(\eta^5-C_5H_4CF_3)(CO)_2]$	2058	2061(sh), 2058	1992	2003, 1992	382
$[Rh(\eta^5-C_5Me_5)(CO)_2]$	2033	2042, 2039	1970	1995, 1979	433
$[Rh(\eta^5-C_5H_5)(CO)_2]$	2052	2058, 2056	1988	2010, 2001, 1994	421
$[Rh(\eta^5-C_5H_4CF_3)(CO)_2]$	2065	2069(sh), 2065	2004	2014, 2004	384
$[Ir(\eta^5-C_5H_5)(CO)(C_2H_4)]$	1987, 1984	2004, 1992			404
PE disc	PE	PE–SO_2	PE	PE–SO_2	PE–SO_2
$[Ir(\eta^5-C_5Me_5)(CO)_2]$	2017	2032, 2022	1949	1979, 1966	427
$[Rh(\eta^5-C_5Me_5)(CO)_2]$	2025	2043, 2033	1960	1992, 1980	

* Data for Ar matrices containing 1.2% SO_2.

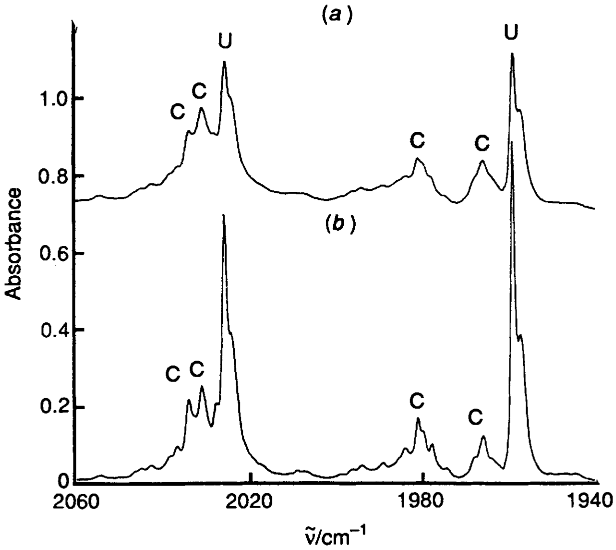

Fig. 2 The IR spectra in the CO-stretching region for $[Ir(\eta^5-C_5Me_5)(CO)_2]$ deposited in a cryogenic matrix (20 K) of argon with (*a*) 1.2 and (*b*) 0.6% SO_2. U = Uncomplexed precursor, C = complex

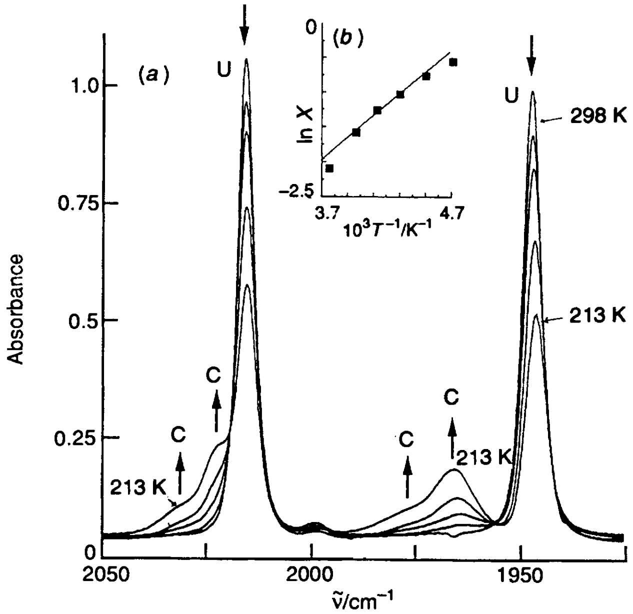

Fig. 3 (*a*) IR spectra for $[Ir(\eta^5-C_5Me_5)(CO)_2]$ deposited in a low density polyethylene disc. The spectra show the growth of bands of complex (C) upon cooling the disc from 298 to 213 K. U = Uncomplexed precursor. (*b*) Van't Hoff plot for the ratio of the integrated absorbances of the bands of $[Ir(\eta^5-C_5Me_5)(CO)_2{\cdot}SO_2]$ and $[Ir(\eta^5-C_5Me_5)(CO)_2]$: ln X against T^{-1} ($X = A_{1949}/A_{1966}$, $\Delta H^0 = -13 \pm 3$ kJ mol^{-1})

and metal: λ_{max} $(\eta^5-C_5Me_5) > (\eta^5-C_5H_5) > (\eta^5-C_5H_4CF_3)$, Rh > Ir.

Similar experiments with $[M(\eta^5-C_5H_5)(C_2H_4)_2]$ (M = Co, Rh or Ir) in 2% SO_2–Ar matrices again reveal prominent UV/VIS absorptions (Co 444, Rh 442, Ir 420 nm). In the case of rhodium, the band is in a different position from that of the established $[Rh(\eta^5-C_5H_5)(C_2H_4)(SO_2-S)]$ complex, showing that we are not observing substitution reactions. The value of λ_{max} is more sensitive to the SO_2 concentration than to that of the carbonyl complex.

In low density polyethylene (PE) discs the SO_2 concentration and the sample temperature can be varied smoothly over a wide range. A solution of the organometallic in heptane or supercritical CO_2 is applied to a PE disc, and the solvent removed *in vacuo*.[5] The disc is mounted in a sealed cell which can be filled with a controlled pressure of SO_2. When $[Ir(\eta^5-C_5Me_5)(CO)_2]$ is treated with 0.3 atm (1 atm ≈ 10^5 Pa) SO_2 at 296 K, weak bands [marked C in Fig. 3(*a*)] appear at 2022 and 1966 cm^{-1}, 5 and 17 cm^{-1} to high frequency of the precursor absorptions respectively. On cooling in steps of *ca.* 10 K, these bands increase in intensity progressively [Fig. 3(*a*)] and shoulders become apparent to high frequency. A similar experiment with UV/VIS detection shows a band at 427 nm which increases in intensity either on cooling [Fig. 1(*b*)], or on increasing the SO_2 pressure. When 0.34 atm SO_2 is applied at 268 K and then pumped away, these IR and UV/VIS bands disappear completely. The process could also be reversed by warming. At higher pressures further bands are formed irreversibly. Comparable IR spectra are obtained on treating a PE disc containing $[Rh(\eta^5-C_5Me_5)(CO)_2]$ with SO_2 (Table 1). The effects of SO_2 on the spectra of $[Ir(\eta^5-C_5Me_5)(CO)_2]$ in PE discs are strikingly similar to the matrix spectra (Table 1). In the PE discs we can be certain that the two components of each IR band arise from independent metal dicarbonyl species since matrix splittings are absent from disc spectra.

The conspicuous UV/VIS bands observed in these experiments point to the formation of charge-transfer complexes of the type $[M(\eta^5-C_5R_5)L_2{\cdot}nSO_2]$. Their positions are very sensitive to the electronic properties of the cyclopentadienyl ring. The bands shift to lower energy on methylating the ring for a given metal as do the ionisation energies of the complexes.[6,7] Conversely they move to higher energy for each metal complex when one hydrogen on the ring is substituted by CF_3. There is also a blue shift on replacing Rh by Ir which matches the increase in ionisation energy of $[Ir(\eta^5-C_5H_5)(CO)_2]$ relative to

[$Rh(\eta^5-C_5Me_5)(CO)_2$].[6] The high frequency shifts of the ν(CO) bands of the carbonyl complexes demonstrate that charge has been transferred from the metal complexes to SO_2. Thus both IR and UV/VIS spectra demonstrate that the metal complex acts as a Lewis base and SO_2 as the acid in the ground state of these complexes.

The enthalpy of complexation may be determined from the temperature dependence of the spectra in PE discs if we assume that the SO_2 is present in constant excess. By measuring the integrated absorbance (A) of the bands of [$Ir(\eta^5-C_5Me_5)(CO)_2$] at 1949 cm^{-1} and its SO_2 complex at 1966 cm^{-1} and plotting ln (A_{1966}/A_{1949}) *vs.* T^{-1} we find that $\Delta H^0 = -13 \pm 3$ kJ mol^{-1} [Fig. 3(*b*)].*

The IR spectra of the carbonyl complexes may be compared to those of the inner-sphere adducts with Lewis acids such as $HgCl_2$ and with the recently described H-bonded complexes with fluoroalcohols.[8,9] However, the charge-transfer complexes with SO_2 may alternatively involve outer-sphere interactions as have been described for numerous other organometallic bases interacting with organic acids.[10] Sulfur dioxide has long been known to act as an acceptor towards main group bases,[11] but the closest analogues may be the c.t. complexes formed between SO_2 and iodide or thiolate ligands on transition metals.[12] The sensitivity of the UV/VIS spectra of some of the complexes to SO_2 concentration suggests that SO_2 aggregates may also play a role as postulated by Kubas.[1] The discovery of c.t. complexes between SO_2 and simple organometallics opens opportunities for many new c.t. complexes† and for atom- or electron-transfer reactions, as well as lending support to Cramer's[2] original mechanism.

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* Measurements of ΔH^0 for the interaction of fluoroalcohols with [$Ir(\eta^5-C_5Me_5)(CO)_2$] proved very similar whether measured in heptane solution or PE discs.[5] This comparison gives confidence that the measurements reported here reflect chemical interaction with SO_2, rather than a polymer property.

† Simple metallocenes and metallocarboranes also form charge-transfer complexes with SO_2.[13]