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PREPARATION AND PROPERTIES OF TWO PENTACARBONYLTUNGSTEN COMPLEXES OF SUBSTITUTED CYCLOPROPENYLIDENES

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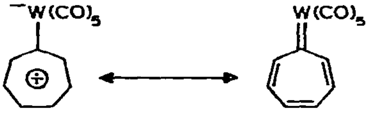
Summary

2,3-Diphenylcyclopropenylidene(pentacarbonyl)tungsten and 2,3,-di-t-butylcyclopropenylidene(pentacarbonyl)tungsten have been prepared by the method of Öfele for comparison with cycloheptatrienylidene, diphenylcarbene and phenylmethoxycarbene complexes of pentacarbonyltungsten. Both the cycloheptatrienylidene and cyclopropenylidene complexes are poorer π-acceptors than the other carbene complexes. Furthermore there is some evidence that cyclopropenylidene is a poorer acceptor than cycloheptatrienylidene although this is not conclusive. Both of the cyclopropenylidene complexes show greater thermal stability and lower chemical reactivity than the cycloheptatrienylidene complex.

We recently reported the synthesis of cycloheptatrienylidene(pentacarbonyl)tungsten [1]. From its dipole moment and spectral properties it was concluded that this complex is dipolar in nature (substantial contribution from resonance from 1a) but is also stabilized by back-bonding as represented by resonance from 1b.



(1a) (1b)

For purpose of comparison we have now synthesized two cyclopropenylidene(pentacarbonyl)tungsten complexes 2 and 3 *.

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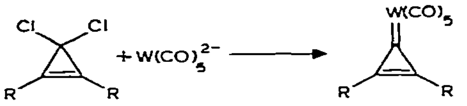
* While this work was in progress, the preparation of 2,3-di-t-butylcyclopropenylidene complexes of h^5-cyclopentadienyldicarbonyliron and $PdCl_2$ were reported [2].

Diphenylcyclopropenylidene(pentacarbonyl)tungsten, II, was synthesized by the procedure developed by Öfele [3] for the synthesis of diphenylcyclopropenylidene(pentacarbonyl)chromium. The necessary dianion ($W(CO)_5^{2-}$) was generated by the method of Ellis [4]. The carbene complex was isolated as bright yellow crystals.



(2, R = Ph
3, R = t − Bu)

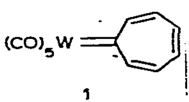
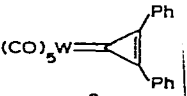
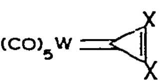
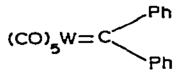
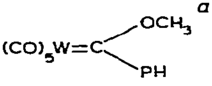
A cyclopropenylidene complex with less perturbation was also desirable. We therefore attempted to apply the same synthetic method to the preparation of the unsubstituted cyclopropenylidene complex. Unfortunately this failed, as did attempts to prepare the diethyl analogue. However, the method was found to be satisfactory for the preparation of 2,3-di-t-butylcyclopropenylidene(pentacarbonyl)tungsten. This complex was isolated as pale yellow needles.

Some of the key physical and spectral properties of 1, 2 and 3 and selected models are summarized in Table 1. From a comparison of the values of π (computed from *cis* and *trans* CO force constants and believed to be a measure of back bonding [7] it is clear that there is less back bonding onto the carbene ligands of 1, 2 and 3 than is the case for either 4 or 5. This is as expected since the aromaticity of the conjugated rings should raise the energy of the LUMO relative to complexes such as 4. Simple HMO would also predict less back bonding into the cyclopropenylidene ring than the cycloheptatrienylidene analogue. In fact, π is somewhat smaller but it is not certain that this difference is significant.

That cyclopropenylidene and cycloheptatrienylidene are poorer π-acceptors than 4 and 5 is also clear from a comparison of dipole moments. Thus, using

TABLE 1

BACK-BONDING AND DIPOLE MOMENTS OF CARBENE COMPLEXES OF PENTACARBONYL TUNGSTEN

	 1	 2	 3	 4 [a]	 5 [a]
k_1 [b]	15.34	15.31	15.29	15.87	15.71
k_2 [b]	15.72	15.73	15.72	16.08	15.90
k_i [c]	0.29	0.31	0.32	0.26	0.31
π [d]	0.30	0.26	0.25	0.47	0.49
Dipole Moment	7.7	8.06	7.71	3.48	4.39
^{13}C chemical shift at the carbene carbon		203 [e]	211.3	358.3	323.9

[a] Data taken from Ref. 6. [b] Force constants of carbonyls (in Millidynes/Ångström). k_1 refers to CO *trans* to the carbene; computed by the method of Cotton and Kraihanzel [6]. [c] Stretch—Stretch interaction constant. [d] Measure of backbonding computed by the method of Graham [7]. [e] For comparison, the cyclopropenyl ring carbon of the triphenylcyclopropenyl carbenium ion appears at 153.2 ppm [8].

the simple approach of Tobey [9] and assuming that 1) the charge on the metal in all the complexes is that same, 2) the positive charge in the diphenylcarbene complex is localized on the carbene carbon (shift of charge onto the phenyl rings would reduce the computed dipole moments of the ring complexes), 3) the negative charge in all complexes is localized on tungsten and 4) the carbene carbon—metal bond length is 2.14 Å in all cases, the maximum dipole moment (computed for charges centered in the rings) expected for the cyclopropenylidene and cycloheptatrienylidene complexes are 4.78 and 6.10 D, respectively. The larger observed moments clearly indicate that both rings have more positive charge than does the carbene carbon of 4. Furthermore, if the positive charges in 1 and 3 are centered in the rings, the dipole moments would indicate a greater back bonding in the cycloheptatrienylidene complex than in its smaller ring relative. However, as pointed out by Tobey [9], due to the energy required to separate charges the positive charge is probably not centered and as a result, a simple comparison of 1 with 2 or 3 is not reliable.

Although not clearly understood [10], the most sensitive probe for d_π—p_π back-bonding from metals onto carbenes is probably the ^{13}C chemical shift of the carbene carbon; the greater the back-bonding the greater the downfield shift. A comparison of 2—5 in Table 1 dramatically demonstrates this effect; for example, the carbene carbon of 4 is shifted over 150 ppm downfield from the corresponding carbon in the diphenylcyclopropenylidene complex. As above, these results clearly demonstrate greater back-bonding into 4 and 5 than 2 and 3. A comparison of the cycloheptatrienylidene complex 1 with 2 and 3 is also desirable. Unfortunately, despite numerous attempts, we have been unable to obtain the chemical shift of the carbene carbon of 1.

A cursory comparison of the chemical properties of 2 and 3 with 1 was also made. It was found that the cycloheptatrienylidene complex is less stable to heat, acid and DMSO than the small ring complexes. For example, whereas 1 is completely destroyed (primarily to heptafulvalene) by refluxing in heptane for one hour, 3 is only one-half decomposed (to unknown products) after two hours under the same condition. Dry HCl also rapidly destroys 1 under conditions (r.t. in CH_2Cl_2) where 3 is stable (90% recovered after two hours). At room temperature, DMSO smoothly converts 1 to tropone. In contrast 2 and 3 are completely stable to this reagent (Ce^{IV} converts 2 to the ketone in 20% yield). Finally, solutions of 1 are sensitive to air and light but solutions of 2 and 3 appear to be stable.

In summary, the physical and spectral properties of 1, 2 and 3 clearly indicate less back bonding than is found in other carbene complexes. They are also consistent with more donation into cycloheptatrienylidene than cyclopenylidene although interpretation of the small differences observed in these cases is somewhat hazardous. Finally the cycloheptatrienylidene complex is more reactive than the small ring complexes. In at least some reactions, this might also be due to differences in back bonding because the reactions may depende on CO loss to give a reactive site.

Experimental section

Tungsten hexacarbonyl was dried over P_2O_5 in a vacuum desiccator. Diphenylcyclopropenone was synthesized by the method of Breslow et al.

[11]. 2,3-Di-t-butylcyclopropenone was synthesized by the method of Ciabattoni and Nathan [12].

HMPA was refluxed over CaH_2 under reduced pressure and distilled. Just before each reaction, a slight excess of the dried HMPA was placed in a flask and a small amount of Na was added. Stirring under Ar produced a blue color. HMPA was directly distilled into a Schlenk tube for reaction. Throughout the following operations an Ar atmosphere was maintained. A glass stirring bar was used.

2,3-Diphenylcyclopropenylidene(pentacarbonyl)tungsten

To a suspension of 1.5 g of $W(CO)_6$ (4.3 mmol) in 40 ml of HMPA (distilled directly from stock prepared as described above) under an argon atmosphere was added an excess of sodium (3~4 equiv.) cut into small pieces. After a few hours the solution turned intense blue when the excess sodium was manually removed and the solution was cooled with an ice bath. A solution of 1.1 g of 1,1-dichloro-2,3-diphenylcyclopropene (4.3 mmol) (prepared from 4.3 mmol of 2,3-diphenylcyclopropenone and 4.7 mmol of oxalyl chloride in methylene chloride) in 10 ml of THF was added dropwise over a 10 min period with a syringe. The resultant dark brown solution was stirred for an additional hour at r.t. and poured into 1 l of saturated aq. NaCl solution followed by extraction with ether three times. The dried organic phase (over sodium sulfate) was concentrated and ca. 5 g of silica gel was added. After complete evaporation of the ether the silica gel was placed on top of a chromatography column (1″ × 2′, ca. 70 g of silica gel) and eluted with pentane-methylene chloride (up to 20%). Isolation of a bright yellow band and recrystallization from methylene chloride gave bright yellow crystals; ca. 10% based on $W(CO)_6$: m.p. 215°C (in sealed tube, decomposition). ^1H NMR (δ, $CDCl_3$) ca. 8.35 (m, 4 H), ca. 7.77 ppm (m, 6 H). IR (KBr) 2064, 1990, 1934, 1600, 1580, 1480 cm^{-1}. ^{13}C NMR (δ, $CDCl_3$) [$Cr(AcAc)_3$] 124.1, 129.8, 132.1, 134.7, 178.3 (vinyl, J 125.1 Hz), 197.2 (*cis*CO), 204.0 (carbene), 206.1 ppm (*trans* CO), UV_{max} heptane 196 (log ϵ 4.96), 242 (log ϵ 4.55), 270sh, 280sh, 351 (log ϵ 3.91), 430sh nm; Anal. Found: C, 46.92; H, 2.01. $C_{20}H_{10}O_5W$ calcd.: C, 46.72; H, 1.96%. Dipole moment (benzene, 26°C); 8.06 D.

2,3-Di-t-butylcyclopropenylidene(pentacarbonyl)tungsten, 3

2,3-Di-t-butylcyclopropenone was dissolved in CH_2Cl_2 (ca. 10 ml/5 mmol of ketone) and treated with 1.1 equiv. of $(COCl)_2$ in CH_2Cl_2 (ca. 10 ml/5 mmol of chloride) at r.t. Gas was immediately evolved and evaporation of solvent left 1,2-di-t-butyl-3,3-dichlorocyclopropene as a clear oil (m.p. is slightly below r.t.).

The resulting solution was cooled briefly in an ice bath and 1 equiv. of the dichloride in 10 ml of dry THF was added dropwise over a 10 min period with a syringe. The ice bath was removed and the resultant solution was stirred for an additional hour and then poured into 1 l of saturated NaCl solution. The aqueous phase was then extracted three times with 200 ml portions of ether. The ether solution was dried over Na_2SO_4, evaporated and the residue was dissolved in a small amount of CH_2Cl_2. A small amount of silica gel thus obtained was placed on the top of a column packed with Baker silica gel

(1" × 2', ca. 70 g) and eluted with pentane-methylene chloride. The first pale yellow band was collected and recrystallized from ether-pentane (cooled slowly to $-70°$C). About 10% analytically pure complex was obtained as pale yellow needles, m.p. 97.5—98.5°C. ^{1}H NMR (δ, $CDCl_3$) 1.45 ppm (s): ^{13}C NMR (δ, acetone-d_6) $[Cr(AcAc)_3]$, 27.7, 34.8, 197.4 (*cis* CO, J 125.7 Hz), 197.7 (vinyl) 211.3 (carbene) 204.0 ppm (*trans* CO). IR_{max} (cyclohexane) 2066, 1969, 1932 cm^{-1}; UV_{max} heptane 240 (log ϵ 4.86), 288 (log ϵ 3.91), 331 nm (log ϵ 4.00); Dipole moment (benzene, 26.5°C) 7.71 D. Anal. Found: C, 40.46; H, 3.86. $C_{16}H_{18}O_5W$ calcd.: C, 40.53, H, 3.83%.

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