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The Titanocene Dicarbonyl Dication [TiCp$_2$(CO)$_2$]$^{2+}$ [†]

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Summary: Two-electron oxidation of TiCp$_2$(CO)$_2$ or double protonation of TiCp$_4$ in toluene under carbon monoxide affords an exceedingly moisture-sensitive solid which has been isolated and identified as the tetraphenylborato derivative of the titanocene dicarbonyl dication [TiCp$_2$(CO)$_2$]$^{2+}$ on the basis of both spectroscopic data and reactivity.

Neutral carbonyl derivatives with the metal in a d^0 or d^{10} electronic configurations are well-known in the literature, selected examples being the cyclopentadienyl-substituted derivatives of zirconium(IV) and hafnium(IV),[1] the halocarbonyls of copper(I), gold(I),[2] and Ag(CO)B(OTeF$_5$)$_4$.[3,4] On the other hand, the first closed-shell, charged carbonyl compound, [Au(CO)$_2$]$^+$, was reported in 1990,[5] followed by the spectroscopic characterization or the isolation of several other compounds of early or late transition metals.[3b,6] For sake of completeness, it is worth mentioning that [Hg(CO)$_2$]$^{2+}$ represents until now the only dicationic metal carbonyl derivative of a d^{10} electronic configuration.[7]

We have now found that the reaction of bis(cyclopentadienyl)dicarbonyltitanium(II), TiCp$_2$(CO)$_2$, with 2 equiv of ferricinium tetraphenylborate in toluene[8] produces a brown solid that is exceedingly sensitive to moisture and whose IR spectrum in the solid state shows two strong carbonyl absorptions at 2119 and 2099 cm^{-1} beyond the absorptions typical of aromatic groups (C$_5$H$_5^-$ and phenyl). A compound with a superimposable infrared spectrum and similar properties has been obtained by the double protonation of TiCp$_4$[9] with 2 equiv of [NH^{n}Bu$_3$]BPh$_4$ in toluene under carbon monoxide (1 atm 25 °C).

On the basis of spectroscopic (IR) and reactivity data (*vide infra*), we suggest that the titanocene dicarbonyl

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dication of formula $[TiCp_2(CO)_2][BPh_4]_2$, **1**, is formed as described in eqs 1 and 2. Compound **1** is thermally

$$TiCp_2(CO)_2 + 2[FeCp_2][BPh_4] \rightarrow \mathbf{1} + 2FeCp_2 \quad (1)$$

$$TiCp_4 + 2[N^nBu_3H][BPh_4] + 2CO \rightarrow \mathbf{1} + 2N^nBu_3 + 2CpH \quad (2)$$

stable and does not lose CO at room temperature, even under high vacuum; on the other hand, rapid evolution of gas and sublimation of BPh_3 is observed by heating **1** *in vacuo*.

Carbon monoxide is readily lost by **1** in the presence of chloride ions: the reaction with PPNCl[10] (PPN = μ-nitridobis(triphenylphosphonium) cation) in toluene gives quantitative yields of $TiCp_2Cl_2$ and PPN[BPh_4], see eq 3. The oxidation state (IV) of titanium in **1** is

$$[TiCp_2(CO)_2][BPh_4]_2 + 2PPNCl \rightarrow TiCp_2Cl_2 + 2PPN[BPh_4] + 2CO \quad (3)$$

further confirmed by the reaction of $[TiCp_2(CO)_2][BPh_4]_2$ with $CoCp_2$ in toluene *under an argon atmosphere*, which gives quantitave yields of $TiCp_2(CO)_2$ and $[CoCp_2][BPh_4]$, see eq 4.[11]

$$[TiCp_2(CO)_2][BPh_4]_2 + 2CoCp_2 \rightarrow TiCp_2(CO)_2 + 2[CoCp_2][BPh_4] \quad (4)$$

Moreover, a suspension of **1** in toluene promptly reacts with water to give $TiCp_2(CO)_2$ (90%, IR analysis), benzene, and biphenyl (GC-MS analysis), suggesting that the Ti(IV) → Ti(II) reduction is promoted by the BPh_4^- anion.[12] The absence of dihydrogen in the gas phase and of carbon dioxide in the toluene solution confirms this suggestion.

Due to the instability to moisture and to basic solvents (CO is promptly evolved on treatment of **1** with THF or acetone) and to the limited solubility in hydrocarbon solvents, we have not been able to grow single crystals of compound **1**; nevertheless, a spectral pattern in the carbonyl stretching region similar to that of $MCp_2(CO)_2$, M = Ti, Zr, Hf,[13] and $[VCp_2(CO)_2]^+$ [14] is observed *i.e.*, two carbonyl stretching vibrations of approximately equal intensity ($A_1 + B_1$ symmetry of the $M(CO)_2$ fragment in a pseudotetrahedral structure). The OC−M−CO angle, calculated[15] on the basis of the integrated areas of the symmetric and asymmetric carbonyl stretching vibrations,[16] is 86.8°, to be compared with 88°[17] as obtained from the Nujol spectrum of $TiCp_2(CO)_2$ ($\tilde{\nu}CO$ =1962 and 1874 cm^{-1}). The decreased interligand angle for **1** is qualitatively in agreement with the increased oxidation state on going from titanium(II) to titanium(IV).

At the best of our knowledge, **1** is the first dicationic metallocene dicarbonyl derivative to be described;[18] moreover, it adds to the still restricted family of the dicationic carbonyl compounds of recent acquisition in the literature.[7,19]

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(8) A suspension of $[FeCp_2][BPh_4]$ (2.54 g, 5.03 mmol) in toluene (50 mL) was saturated with CO, and solid $TiCp_2(CO)_2$ (0.59 g, 2.52 mmol) was added. After 72 h of stirring at room temperature, a suspension of a brown solid in an orange solution was obtained. An IR spectrum of the solution showed no absorptions due to $TiCp_2(CO)_2$. The suspension was filtered, and the brown solid was washed with toluene until the washings were almost colorless (5 × 5 mL). After the solid was dried *in vacuo* at room temperature, the compound (1.56 g, 69% yield) was identified as $[TiCp_2(CO)_2][BPh_4]_2$. Anal. Calcd for $C_{60}H_{50}B_2O_2Ti$: C, 82.6; H, 5.8; CO, 6.4. Found: C, 82.5; H, 6.0; CO, 6.3. IR (Nujol/polychlorotrifluoroethylene): $\tilde{\nu}$ = 3093 (m), 3053 (m-s), 2119 (s), 2099 (s), 1951 (vw), 1880 (vw), 1772 (vw), 1591 (m), 1582 (m-w), 1480 (m), 1430 (m-s), 1376 (m), 1332 (m), 1263 (m), 1240 (m), 1185 (w), 1157 (w), 1108 (w), 1068 (w), 1031 (m), 1019 (m), 885 (m-w), 834 (s), 817 (s), 773 (w), 746 (s), 735 (s), 708 (vs), 675 (m), 639 (w), 614 (w), 604 (m) cm^{-1}. The orange solution was evaporated to dryness under reduced pressure at room temperature, and the residue afforded $FeCp_2$ (0.66 g, 70% yield) by sublimation (0.05 mmHg, 40 °C).

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(10) A suspension of PPNCl (0.59 g, 1.03 mmol) in toluene (25 mL) was treated with solid $[TiCp_2(CO)_2][BPh_4]_2$ (0.46 g, 0.52 mmol). The initially brown suspension gave a colorless solid and a red-orange solution after 15 h of stirring at room temperature. The suspension was filtered, and the solid was washed with toluene (6 × 3 ml), dried *in vacuo*, and identified as PPN[BPh_4] (0.6 g, 68% yield) from its IR spectrum. The solution was dried *in vacuo* at room temperature affording 0.11 g (85% yield) of $TiCp_2Cl_2$, identified by IR and NMR techniques. A gas volumetric control of the reaction showed that the treatment of **1** with PPNCl in toluene at 26.8 °C causes CO evolution up to a CO/Ti molar ratio of 1.98.

(11) A suspension of $[TiCp_2(CO)_2][BPh_4]_2$ (0.38 g, 0.43 mmol) in toluene (10 mL) was treated with solid $CoCp_2$ (0.17 g, 0.90 mmol). After 1 h of stirring at room temperature, an IR spectrum of the solution showed the presence of $TiCp_2(CO)_2$ ($\epsilon_{1885} = 2200\ M^{-1}\ cm^{-1}$, 98% yield). The suspension was filtered, and the yellow solid was washed with toluene (3 mL), dried *in vacuo*, and identified as $[CoCp_2][BPh_4]$ (0.32 g, 69% yield) from its IR spectrum.

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