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Synthesis and IR Spectroelectrochemical Studies of a [60]Fulleropyrrolidine-(tricarbonyl)chromium Complex: Probing C_{60} Redox States by IR Spectroscopy

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The synthesis of a new fulleropyrrolidine-(tricarbonyl)chromium complex: 1-methyl-2-(4-methoxyphenyl)-3,4-[60]fulleropyrrolidine-(tricarbonyl)chromium is described together with its characterization by IR, NMR and cyclic voltammetry. IR spectro-electrochemistry has been used to probe the redox level of the fullerene derivative via the relative position of the vibrational bands of the CO ligands, which are sensitive to the electronic state of the complex. Other strategies to incorporate a tricarbonylchromium moiety to fullerene C_{60} are also briefly discussed and evaluated.

Introduction

Fullerenes have emerged as widely used molecular building blocks in the field of artificial photosynthesis and light-harvesting devices. In this regard, the general interest in fullerenes originates from their rich redox chemistry and low reorganization energy which, in combination, makes them attractive as electron acceptors.[1] Since the discovery of C_{60} in 1985, great advances in fullerene chemistry has permitted the efficient preparation of numerous fullerene-based donor-acceptor systems, many of which have been studied in terms of photo-induced electron transfer.[2] Most such assemblies have electron donors based on transition metal complexes such as ruthenium complexes, metalloporphyrins, phthalocyanines and ferrocene,[2] and the strong donor capability of bis(arene)chromium complexes makes also this group of compounds interesting for the use in donor–acceptor systems with C_{60} as acceptor.[3] The air sensitivity of bis(arene)chromium compounds and complicated preparation routes however limits the usefulness in this context. In contrast, monoarene-(tricarbonyl)-chromium complexes are relatively stable, and can be synthesized and manipulated by regular "wet chemistry" methods.[4] Also arene-(tricarbonyl)chromium complexes are electron donors and have, for instance, been shown to form charge-transfer complexes with acceptors such as 1,3,5-trinitrobenzene and tetracyanoethylene.[5] These properties make also this group of compounds interesting for the use in combination with electron acceptors such as C_{60}. Even more interesting is the fact that the CO ligands may serve as sensitive probes to electronic effects. This has been well established throughout extensive studies by IR spectroscopy, which have shown that the frequency of the CO bands is affected by the electron density on the ligating aromatic ring via back-bonding from chromium to the carbon monoxide ligands.[5] While fullerene anions are generally monitored by NIR spectroscopy via their absorption around 1080 nm for $C_{60}{}^{1-}$ and 945 nm for $C_{60}{}^{2-}$, we were interested in whether IR spectroscopy could be a complimentary technique where the carbonyl absorption frequency could be used to probe different redox states of the C_{60} part of the complex.[6]

There are in principle three different ways to link a tricarbonylchromium moiety to C_{60}: *i*. Direct complexation of $Cr(CO)_3$ to pristine C_{60} to yield a fullerene η^6 complex, *ii*. direct complexation of $Cr(CO)_3$ to a modified fullerene that, in the carbon cage, possess a cyclopentadienyl or phenyl unit isolated from the fullerene π system by sp^3 carbons, i.e. $C_{60}R_5$ or $C_{60}R_6$, and *iii*. complexation of $Cr(CO)_3$ to a phenyl unit attached as an addend to the fullerene cage. To the best of our knowledge no η^6-metal complexes of pristine C_{60} (category *i*) has been reported so far. This is probably due to the curvature of the six-membered rings which prevents efficient orbital overlap between the metal and the π-system.[7] On the other hand, fullerene metal complexes such as $M(\eta^5\text{-}C_{60}R_5)L_n$ have been successfully synthesized (category *ii*) with several group 6–10 metals including chromium.[3d,8] In these complexes the ligating five-membered ring have similar properties as a regular cyclopentadienyl ligand since all five carbon atoms, are

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bonded to sp^3 carbons of the fulleride. The properties of the fulleride parts in this group of complexes are significantly different from pristine C_{60}. In contrast, the properties of fullerene monoadducts moieties of complexes belonging to category *iii* should be relatively similar to that of pristine C_{60}. Furthermore, this route may be less synthetically demanding. Already in 1995 Nefedova et al. reported the synthesis of a tricarbonylchromium complex of diphenylmethanofullerene, prepared by addition of an organometallic diazonium salt to C_{60}.[3c] This is still, as far as we know, the only example of this kind. In the current paper we give an account of our synthetic studies towards category *iii* fullerene-tricarbonylchromium complexes. In this study we have evaluated the possibility to attach tricarbonylchromium units to C_{60} by adapting some recently reported derivatization methods. One new fulleropyrrolidine tricarbonylchromium complex was successfully prepared and characterized spectroscopically as well as by electrochemical and IR spectroelectrochemical methods.

Results and Discussion

Fullerene adducts Cr(**1**)–Cr(**3**) (Figure 1) were suggested as suitable category *iii* targets, each with a slightly different distance between the fullerene and the tricarbonylchromium moiety.

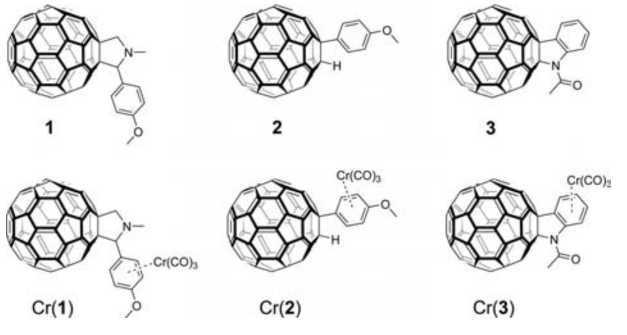
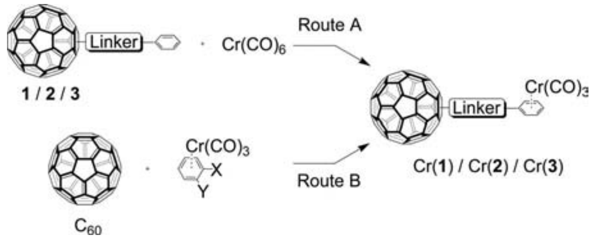


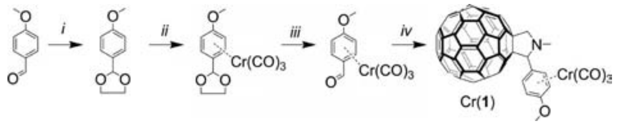
Figure 1. Fullerene derivatives **1**–**3** and their tricarbonylchromium complexes Cr(**1**) to Cr(**3**).

The most straightforward synthesis of any of these compounds would be by direct complexation of tricarbonylchromium to the parent compounds **1**–**3** (Scheme 1, route A). The established procedure to prepare tricarbonylchromium arene derivatives is based on refluxing the arene with $Cr(CO)_6$ in Bu_2O/THF or decalin for several hours. While this works well for small electron-rich aromatic compounds such as anisole, we were unsuccessful in preparing any of the target compounds by this method despite numerous attempts and various modifications of the reaction conditions. All attempts to prepare Cr(**1**) directly from compound **1** resulted in decomposition of the fulleropyrrolidine, while the attempted synthesis of Cr(**2**) from compound **2** did not result in any reaction at all. With these results in hand we decided to explore the new, more convergent approach where a pre-formed tricarbonylchromium arene compound is coupled to the fullerene (Scheme 1, route B).



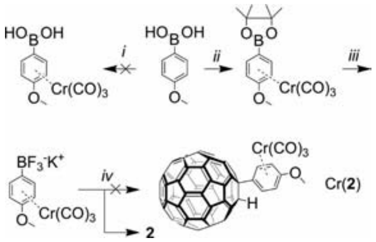
Scheme 1. General strategies to prepare fullerene-tricarbonylchromium complexes Cr(**1**) to Cr(**3**).

Fulleropyrrolidine synthesis via a 1,3-dipolar cycloaddition to C_{60} is among the most versatile fullerene functionalization reactions, and the robustness of this reaction was further proven by the successful preparation of Cr(**1**) in an isolated yield of 27% from 4-methoxybenzaldehyde-(tricarbonyl)chromium, sarcosine and C_{60}. Since tricarbonylchromium complexes are most easily formed with electron-rich aromatics, we chose an aldehyde component derived from anisole. This allowed the preparation of 4-methoxybenzaldehyde-(tricarbonyl)chromium in a yield of 51% over three steps, with hydrolysis of 2-(4-methoxyphenyl)-1,3-dioxolane-(tricarbonyl)chromium[9] immediately before the pyrrolidination step (Scheme 2). Purification of Cr(**1**) was successfully achieved by repeated column chromatography. The purified product could be exposed to air for short periods (hours) without any signs of decomposition. Furthermore, the compound could be stored in a freezer for several weeks under nitrogen atmosphere before decomposing into **1** by dissociation of tricarbonylchromium.



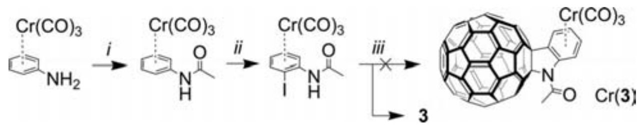
Scheme 2. Synthesis of 1-methyl-2-(4-methoxyphenyl)-3,4-[60]fulleropyrrolidine-(tricarbonyl)chromium [Cr(**1**)]; *i*. 1,2-ethanediol, *p*-toluenesulfonic acid, yield 95%; *ii*. $Cr(CO)_6$, *n*-butyl ether, THF, reflux 12 h, yield 60%; *iii*. HCl, ethanol, room temp., 4 h, yield 90%; *iv*. C_{60}, sarcosine, toluene, reflux 12 h, yield 27%.

The synthesis of hydroarylated fullerene adducts such as **2** was recently reported by Itami et al. The reaction is a palladium or rhodium mediated coupling between an aromatic boronic acid and C_{60}.[10] With this procedure in mind we attempted the complexation of tricarbonylchromium to 4-methoxyphenyl boronic acid with the intention to obtain a chromium complex possible to couple to C_{60} (Scheme 3). However, the isolated product was the tricarbonylchromium complex of anisole, formed by protodeboronation, a reaction that has previously been described for similar systems.[11] In contrast, we were successful in preparing the tricarbonylchromium complexes of the pinacol-protected boronic acid and of 4-methoxyphenyl trifluoroborate. Unfortunately, all attempts of rhodium- or palladium-mediated coupling of these compounds to C_{60} only gave the parent fulleropyrrolidine adduct **2** and the protodeboronation product anisole-(tricarbonyl)chromium.



Scheme 3. *i*. $Cr(CO)_6$, decalin or *n*-butyl ether, THF, reflux 12 h, yield 0%; *ii*. a) pinacol, $MgSO_4$, CH_2Cl_2, reflux 12 h, yield 95%. b) $Cr(CO)_6$, *n*-butyl ether, THF, reflux 12 h, yield 85%; *iii*) KHF_2, methanol, H_2O, stirring 2 h, yield 75%; *iv*) C_{60}, $Rh(cod)_2BF_4$ or Pd catalyst,[10] 1,2-dichlorobenzene, H_2O, 80 °C, 12 h, yield of Cr(**2**): 0%.

The synthesis of fulleroindolines via palladium-mediated coupling of anilines and *o*-iodoanilines to C_{60} was very recently reported by Zhu and Wang.[12] In an attempt towards Cr(**3**), *N*-phenylacetamide-(tricarbonyl)chromium was prepared by acylation of aniline-(tricarbonyl)chromium (Scheme 4). The reported palladium-assisted procedure for coupling of *N*-phenylacetamide to C_{60} did for our chromium complex not give the desired product. Also 2-iodo-*N*-phenylacetamide-(tricarbonyl)chromium, prepared via ortholithiation and a potentially better starting material[12a] did not yield the desired Cr(**3**), but the metal-free parent compound **3**.



Scheme 4. *i*. Acetic anhydride, pyridine, stirring 12 h, yield 85%. *ii*. *n*-butyllithium (2.5 M), 1,2-diiodoethane, THF, –79 °C → r.t., yield 46%. *iii*. C_{60}, $Pd(OAc)_2$, DABCO, PPh_3, 130 °C, 12 h, yield of Cr(**3**): 0%.

An obvious conclusion from these attempts is that the tricarbonylchromium arene components are not compatible with the conditions for palladium and rhodium mediated arene-C_{60} couplings used in our attempted synthesis of compounds Cr(**2**) and Cr(**3**), whereas the cycloaddition route to Cr(**1**) was successful.

Characterization

The IR spectrum of Cr(**1**) in its solid state shows two strong bands for the CO groups at 1957 and 1876 cm^{-1}, typical of a tricarbonylchromium complex (Figure 2). As a comparison, the CO bands of anisole-(tricarbonyl)chromium are positioned at 1940 and 1837 cm^{-1}.

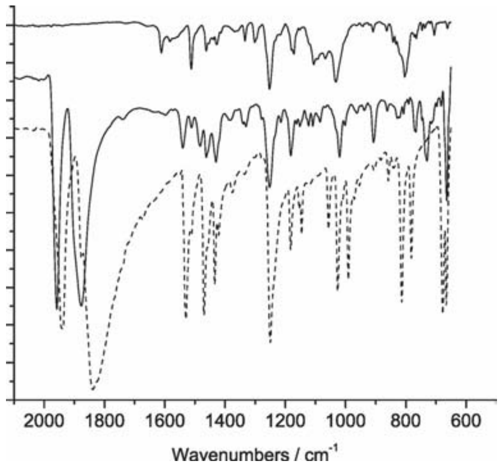


Figure 2. IR spectra (neat) of compound **1** (upper), compound Cr(**1**) (middle), and anisole-(tricarbonyl)chromium (lower).

The ^1H NMR spectrum of Cr(**1**) in $CDCl_3/CS_2$ (Figure 3) display chemical shifts in the aromatic region typical of aromatic tricarbonylchromium complexes.[13] In 1-methyl-2-(4-methoxyphenyl)-3,4-[60]fulleropyrrolidine (compound **1**) the aromatic proton signals are at $\delta = 7.95$ and 7.70 ppm, whereas in Cr(**1**), the signals appears at 6.2–5.1 ppm. Moreover, all four aromatic protons in Cr(**1**) are chemically non-equivalent and have different chemical shifts, suggesting hindered rotation of the aromatic ring.

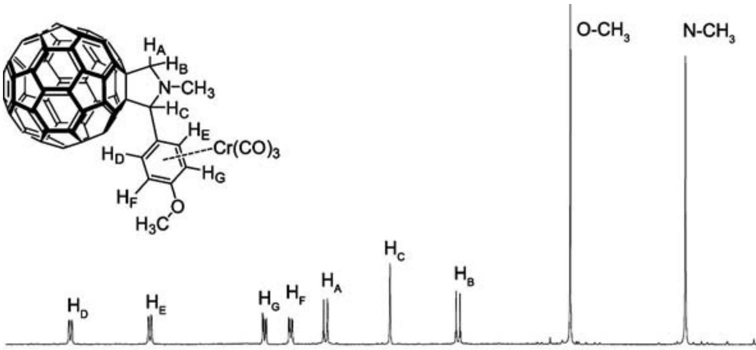


Figure 3. ^1H NMR spectrum (500 MHz, $CDCl_3/CS_2$, 25 °C) of Cr(**1**).

The ^{13}C NMR spectrum of the compound (see Supporting Information) shows a large shift to lower frequencies of between 30–45 ppm for the aromatic CH carbons in Cr(**1**) as compared to the corresponding atoms in **1**. As expected, only one signal for the three carbon monoxide ligands could be observed at $\delta = 232.4$ ppm at room temperature, suggesting a low energy barrier for rotation about the metal-arene bond, despite the relatively close proximity to C_{60} in the molecule. This low barrier was confirmed by low-temperature ^{13}C NMR measurements which showed a single (broad) carbonylic signal at temperatures as low as –95 °C, indicating a very low energy barrier of rotation, and thus, a fast equilibrium exist between the different conformers.

Electrochemistry

Cyclic voltammetry of Cr(**1**) (0.3 mM) carried out in CH_2Cl_2 shows one irreversible oxidation taking place at 0.40 V vs. Fc/Fc$^+$, which can be assigned to the one-electron oxidation of the $Cr(CO)_3$ unit (Figure 4). This is confirmed by the reference voltammogram of 2-(4-methoxyphenyl)-1,3-dioxolane-(tricarbonyl)chromium which shows one irreversible oxidation at the same potential.

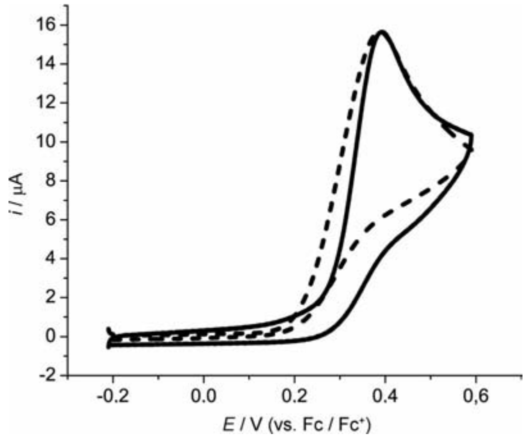


Figure 4. Voltammograms (oxidation scan) for Cr(**1**) (0.3 mM) (solid line) and 2-(4-methoxyphenyl)-1,3-dioxolane-(tricarbonyl)chromium (dashed line).

The reduction scan of compound Cr(**1**) on the other hand shows several reductions, where at least the first two reductions at –1.14 and –1.54 V vs. Fc/Fc$^+$ are electrochemically reversible (Figure 5 and Supporting Information). Unfortunately, we were unable to determine the electrochemical reversibility of the later C_{60} reductions due to the instability of fullerene-trianions in CH_2Cl_2,[14] which among the solvents tried out was the one where all compounds were soluble enough.

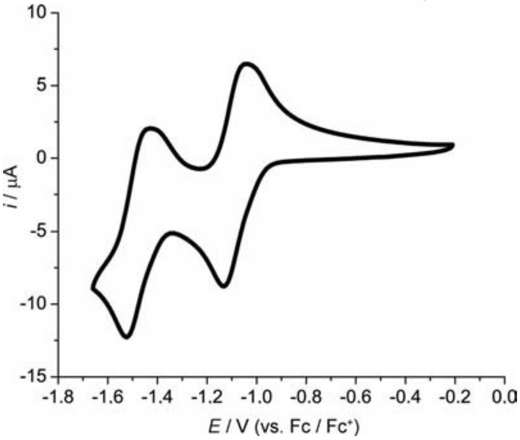


Figure 5. Voltammogram of compound Cr(**1**) (0.3 mM). Reduction scan showing the two first reductions of Cr(**1**).

With the reduction potentials known, we were interested in if we could use IR spectroscopy to probe the redox states of the fullerene in Cr(**1**) by monitoring the vibrational frequency of the CO ligands. This would then also give information about the electronic coupling between the tricarbonylchromium and the fullerene moiety. Therefore, a number of IR spectroelectrochemical measurements were carried out, in which the various anions of Cr(**1**) were generated stepwise by controlled potential bulk electrolysis in CH_2Cl_2 under inert conditions, and monitored by IR spectroscopy. Figure 6 shows the carbonylic region of the IR spectra of compound Cr(**1**) at different redox states. The frequencies of the two carbonylic bands in the neutral complex are found at 1965 and 1888 cm^{-1}. Upon reducing the complex to its anionic state $[Cr(\mathbf{1})]^{1-}$, these bands are red shifted to 1962 and 1883 cm^{-1}. Further reduction of the complex to its dianionic state $[Cr(\mathbf{1})]^{2-}$ leads to an additional shift of the bands to 1961 and 1880 cm^{-1}, respectively.

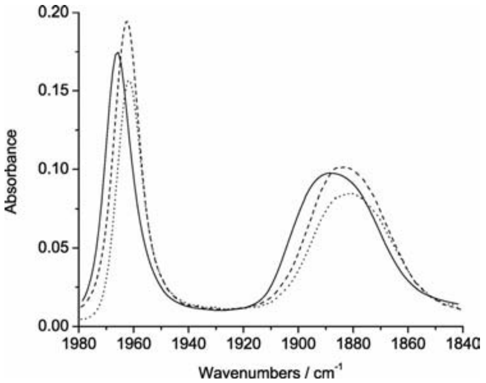


Figure 6. Expansion of the carbonylic region of the IR spectra of compound Cr(**1**) at different redox states: neutral complex (solid), $[Cr(\mathbf{1})]^{1-}$ (dashed), $[Cr(\mathbf{1})]^{2-}$ (dotted).

Importantly, reoxidation of the complex from both the anion and dianion to its neutral state is accompanied by a blue shift of the bands to their original position indicating further the electrochemical reversibility of these processes. Furthermore, bulk electrolysis provided additional information about the electrochemical processes and showed, in agreement with the results from cyclic voltammetry and IR spectroelectrochemistry, a high electrochemical reversibility for the first two redox events (see Supporting Information).

Together, the results suggest a certain degree of communication between C_{60} and the tricarbonylchromium moiety. The red shift of the CO frequencies upon reduction of the complex is caused by increased back-bonding from the chromium to the carbon monoxide, which results in a slight decrease in C–O bond strength for the three carbon monoxide ligands. It is noteworthy that the lower frequency IR band around 1880 cm^{-1} is more sensitive to electronic effects than the band around 1965 cm^{-1} suggesting a preferential use of this band to probe redox processes going on in the system. In this sense, the redox level of compound Cr(**1**) can be determined via the relative position of the vibrational frequencies, ν(CO), in the complex. According to our measurements this is manifested by ν(CO) = 1888 cm^{-1} for the neutral complex, ν(CO) = 1883 cm^{-1} for [Cr(**1**)]$^{1-}$ and ν(CO) = 1880 cm^{-1} for the dianion, [Cr(**1**)]$^{2-}$. It is furthermore possible that this methodology could be used to probe higher fullerene anions, but in that case another solvent than CH_2Cl_2 has to be used.[14]

Conclusions

We have evaluated some methods to attach arene-(tricarbonyl)chromium units to fullerene C_{60} and successfully prepared a new fulleropyrrolidine-(tricarbonyl)chromium complex via a 1,3-dipolar cycloaddition involving a tricarbonylchromium arene aldehyde as one of the reactants. In contrast, we were unable to prepare tricarbonylchromium arene complexes of C_{60} by direct complexation to arene-functionalized C_{60} or by adapting reported transition-metal mediated arene-C_{60} coupling methods. The successfully prepared fulleropyrrolidine-(tricarbonyl)chromium complex has been characterized by ^{1}H NMR and ^{13}C NMR, cyclic voltammetry, bulk electrolysis and IR spectroscopy and was found to be chemically and electrochemically stable. IR spectroelectrochemistry revealed a clear dependence of the CO frequencies on the redox state of the C_{60} part of the complex and hence communication between the C_{60} and the tricarbonylchromium moiety is proven. It was further found that IR spectroscopy can be efficiently used to probe the redox states of the fulleropyrrolidine via the relative frequencies of the carbon monoxide ligands in the complex, which red-shifts as the complex is reduced.

Experimental Section

General: Thin-layer chromatography analyses were performed on pre-coated Merck silica gel plates (60 F_{254}) and visualized with UV light. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 500 MHz spectrometer and chemical shifts are given in ppm (δ) using the residual $CHCl_3$ peak as internal standard. Solid state IR spectra were recorded on a Perkin–Elmer Spectrum-100 FT-IR spectrometer with an ATR accessory. The samples were analyzed by placing neat samples directly on the ATR crystal. Solution state IR was performed using a Perkin–Elmer FT-IR spectrometer. UV spectra were recorded on a Varian Cary 3 Bio UV/Vis spectrometer.

2-(4-Methoxyphenyl)-1,3-dioxolane: 4-Methoxybenzaldehyde (5 g, 36 mmol), ethylene glycol (5 g, 80 mmol), *p*-toluenesulfonic acid monohydrate (50 mg, 0.26 mmol) and toluene (50 mL) was added to a round-bottomed flask equipped with a Dean–Stark trap with a condenser. The solution was heated to 145 °C and refluxed overnight. The solution was washed with NaOH (0.1 M), and the organic phase was collected. Toluene was removed in vacuo and the crude product was purified by distillation. Purified yield 6.2 g, 95%, white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.41 (AA′, 2 H), 6.90 (BB′, 2 H), 5.76 (s, 1 H), 4.13 (m, 2 H), 4.02 (m, 2 H), 3.81 (s, 3 H) ppm.

2-(4-Methoxyphenyl)-1,3-dioxolane-(tricarbonyl)chromium: 2-(4-Methoxyphenyl)-1,3-dioxolane (0.8 g, 4.4 mmol), $Cr(CO)_6$ (1.4 g, 6.4 mmol) was added to a three-necked flask equipped with a condenser and the flask was flushed with nitrogen. Degassed *n*-butyl ether (20 mL) was added to the flask via syringe through a septum and the solution was then heated to 160 °C and refluxed for one hour. Degassed dry THF (6 mL) was added and also used to flush sublimed $Cr(CO)_6$ back down into the solution. The solution was refluxed at 160 °C overnight. The yellow solution was then evaporated and the residue was redissolved in ethyl acetate. The heterogeneous solution was filtered through a plug of silica to remove green chromium by-products. The crude product was then subjected to column chromatography (pentane/EtOAc, 10:1) giving pure 2-(4-methoxyphenyl)-1,3-dioxolane chromium tricarbonyl as yellow solid, yield 0.9 g, 65%. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.75 (AA′, 2 H), 5.49 (s, 1 H), 5.08 (BB′, 2 H), 4.12 (m, 2 H), 3.99 (m, 2 H), 3.72 (s, 3 H) ppm.

4-Methoxybenzaldehyde-(tricarbonyl)chromium: 2-(4-Methoxyphenyl)-1,3-dioxolane-(tricarbonyl)chromium (218 mg, 0.7 mmol), HCl (37%, 1 mL) and ethanol (99%, 15 mL) was added to a round-bottomed flask and the mixture was stirred at room temp. under nitrogen atmosphere for 4 h after which TLC showed that all starting material had been consumed. The solvent was evaporated and the crude product was chromatographed on basic Al_2O_3 (pentane/EtOAc) to yield the pure product as an orange solid; yield 173 mg, 92%. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 9.39 (s, 1 H), 6.06 (AA′, 2 H), 5.19 (BB′, 2 H), 3.80 (s, 3 H) ppm.

1-Methyl-2-(4-methoxyphenyl)-3,4-[60]fulleropyrrolidine-(tricarbonyl)chromium [Cr(1)]: C_{60} (80 mg, 0.1 mmol), 4-methoxybenzaldehyde-(tricarbonyl)chromium (30 mg, 0.1 mmol) and sarcosine (18 mg, 0.2 mmol) was added to a round-bottomed flask equipped with a condenser. Degassed toluene (60 mL) was added and the solution was refluxed at 130 °C overnight under nitrogen atmosphere. The solvent was evaporated and the residue was chromatographed on silica using dichloromethane as eluent. The product was obtained as a brown solid, yield 30 mg, 27%. ^{1}H NMR (500 MHz, $CS_2/CDCl_3$, 25 °C): δ = 6.18 (dd, J = 7.2, 1.9 Hz, 1 H, H_D), 5.78 (dd, J = 7.2, 1.9 Hz, 1 H, H_E), 5.22 (dd, J = 7.1, 2.3 Hz, 1 H, H_G), 5.09 (dd, J = 7.1, 2.3 Hz, 1 H, H_F), 4.96 (d, J = 9.7 Hz, 2 H, H_A), 4.64 (s, 1 H, H_C), 4.31 (d, J = 9.7 Hz, 2 H, H_B), 3.73 (s, 3 H, O-CH_3), 3.15 (s, 3 H, N-CH_3) ppm. ^{13}C NMR (125 MHz, $CS_2/CDCl_3$, 25 °C): δ = 232.4, 155.6, 153.4, 151.8, 147.4, 147.3, 146.34, 146.30, 146.25, 146.20, 146.12, 146.10, 146.0, 145.7, 145.6, 145.55, 145.4, 145.37, 145.30, 145.27, 145.18, 145.15, 144.7, 144.5, 144.4, 144.2, 143.1, 143.05, 142.8, 142.66, 142.61, 142.4, 142.20, 142.14, 142.12, 142.05, 141.9, 141.7, 141.67, 141.62, 140.4, 139.9, 139.4, 136.9, 136.3, 136.1, 135.4, 128.3, 101.3, 93.3, 91.7, 79.1, 78.1, 71.2, 67.7, 55.5, 41.0 ppm. FT-IR (neat): $\tilde{\nu}$ = 2952, 2916, 2848, 2783 (C–H), 1960, 1877 ($C\equiv O$), 1538, 1482, 1461, 1430, 1252, 1178, 1020, 904, 768, 731, 666 cm^{-1}. $C_{73}H_{13}CrNO_4 \cdot H_2O$ (1037.04): calcd. C 84.48, H 1.44, N 1.35; found C 84.29, H 1.49, N 1.37.

Electrochemistry: Cyclic voltammetry and controlled potential electrolysis were carried out in an inert atmosphere in a glovebox by using an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie). Sample solutions (4 mL) were prepared from dry CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (Fluka, electrochemical grade) as supporting electrolyte. For cyclic voltammetry, the working electrode was a glassy carbon disc (diameter 3 mm). All cyclic voltammograms shown were recorded at a scan rate of 0.1 V s^{-1}. A glassy carbon rod served as counter electrode, and the reference electrode was a Ag/Ag^+ electrode (a silver wire immersed into 10 mM $AgNO_3$ in acetonitrile) with a potential of –0.07 V vs. the ferrocene/ferrocenium (Fc/Fc^+) couple in dry CH_2Cl_2. The counter and reference electrode were in compartments separated from the bulk solution by fritted disks and were the same for all analytical, bulk and spectroelectrochemical experiments. Before all measurements, oxygen was removed by bubbling solvent-saturated argon through the stirred solutions. Samples were kept under argon during measurements. To obtain IR spectra of Cr(**1**) in different oxidation states, solutions prepared in the same way as described above for analytical electrochemistry were subjected to bulk electrolysis at controlled potentials. A cylindrical platinum grid (4 cm^2) was used as working electrode for bulk electrolysis. The electrolysis experiments were monitored by amperometry and coulometry and took 3–5 min to completion. After electrolysis, aliquots of 100 µL were taken from the solution, with an air-tight, argon-filled syringe, transferred to an argon-flushed IR-cell with CaF_2 windows which was sealed inside the glovebox before transferred to the IR spectrometer.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of compound Cr(**1**), additional voltammogram of compound Cr(**1**) and IR spectra, details on bulk electrolysis and UV/Vis spectra are given.

Acknowledgments

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