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Photochemically Generated Organometallic Molecular Square Complexes

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Introduction

Research in our group has been focused on the applications of photochemistry to the synthesis of novel organometallic compounds.[1,2] Photochemistry offers a simple, and often highly selective, route to organometallic compounds, overcoming large enthalpy barriers. As a consequence, it is often possible to prepare complexes that are otherwise inaccessible by conventional thermochemical routes.[3] In addition, in many cases known complexes can be prepared far more efficiently and rapidly using photochemistry as compared to thermochemistry.[4] In this note we show how organometallic photochemistry can be used for the assembly of novel organometallic molecular square complexes, efficiently, selectively, and in high yield. The area of metal-containing molecular square complexes has been pioneered by Fujita,[5−7] and our contribution comes at a time of increased research effort to prepare more inorganic and organometallic complexes of this type for application in host−guest, inclusion, and molecular recognition chemistry. This is evidenced by the number of recent reviews discussing the topic.[8−10]

Results and Discussion

The molecular squares were prepared by first generating corner fragments and then reacting them with further equivalents of metal fragment, the whole process being performed photochemically (Scheme 1). Irradiation of a dichloromethane solution of $M(CO)_6$ (M = Cr, Mo) and the ditopic, nonchelating ligand 4,4′-bipyridine (4,4′-bipy) in a 1:2 ratio leads to the *cis*-disubstituted complex $M(CO)_4(4,4'\text{-bipy})_2$ [M = Cr (**1**), Mo (**2**)] in quantitative yield. Subsequent photolysis of $M(CO)_6$ and **1** or **2** in a 1:1 ratio leads to the formation of the homometallic or heterometallic molecular squares $\{Cr(CO)_4(4,4'\text{-bipy})\}_4$ (**3**), $\{Mo(CO)_4(4,4'\text{-bipy})\}_4$ (**4**), and $\{(CO)_4Cr(4,4'\text{-bipy})Mo(CO)_4(4,4'\text{-bipy})\}_2$ (**5**) between 65 and 75% yield. The new complexes have been characterized by IR, UV, NMR, and, in the cases of **4** and **5**, mass spectroscopic techniques. As the squares are unstable and stick to silica, they could not be purified by column or thin-layer chromatography. Instead, the squares were purified using preferential solvation. The starting materials are soluble in hexane, but the squares are soluble only in dichloromethane. Hence, washing the solid product mixture with hexane and then with dichloromethane leads to an effective purification of the squares. IR and NMR analysis of the squares shows that the reaction is highly selective producing only the desired product since no peaks due to byproducts are observed. It is as a consequence of the stability problems that it has not been possible to obtain confirmatory mass data for **3** either by mass spectroscopy or osmometry as decomposition occurred in all cases.

The squares are all air, moisture, and solvent sensitive at room temperature, those containing chromium exhibiting the greatest tendency toward thermal decomposition. This is not totally unexpected, the instability of group 6 metal carbonyl−polypyridine complexes having being discussed on a number of occasions previously.[11−13] In the absence of scavenging ligands, the molecular squares decompose irreversibly into $M(CO)_4(4,4'\text{-bipy})_2$ and undefined insoluble metal-containing products. However, if 4,4′-bipyridine is added to the solution of the molecular square, $M(CO)_4(4,4'\text{-bipy})_2$ is formed in greater amounts.

The formation of the molecular squares has been monitored by IR spectroscopy. Upon addition of an stoichiometric equivalent of $M(CO)_6$ to a solution of $M(CO)_4(4,4'\text{-bipy})_2$, signals due to both species are clearly seen in the IR spectrum. As the photolysis takes place, the signals due to $M(CO)_4(4,4'\text{-bipy})_2$ remain while those due to $M(CO)_6$ are seen to decrease. At the same time, signals due to a monosubstituted $M(CO)_5(4,4'\text{-bipy})$ species appear, these most probably due to formation of $(CO)_5M(4,4'\text{-bipy})M(CO)_4(4,4'\text{-bipy})$ and $(CO)_5M(4,4'\text{-bipy})M(CO)_4(4,4'\text{-bipy})M(CO)_5$. As time passes, the signals for the monosubstituted species decrease and those corresponding to bis-substituted metal centers increase until they are the only feature in the ν_{CO} region of the spectrum, indicating formation of the square.

The coordinated 4,4′-bipyridine ligands in **3** and **4** display only two signals in the ^1H NMR and four in the $^{13}C\{^1H\}$ NMR spectrum (one for CO groups and three for 4,4′-bipy ligands) as predicted for these symmetrical species. All the signals are shifted slightly downfield compared to 4,4′-bipyridine, those corresponding to the *ortho* carbons and hydrogens being the greatest affected. The heterometallic square **5** shows four signals in the ^1H NMR (8.91, 8.85, 7.56, and 7.53 ppm) and eight in the $^{13}C\{^1H\}$ NMR spectrum (two for CO groups and six for 4,4′-bipy ligands) illustrating the lower symmetry of the square. The multiplets at 7.56 and 7.53 ppm in the ^1H NMR spectrum are assigned to the protons *meta* to the ring nitrogens, and although these sets of protons are symmetrically nonequivalent, the two multiplets are almost superimposed on one another and there is only a small change in splitting pattern and in chemical shift as compared to the comparable multiplet in the free ligand. The multiplets corresponding to the protons *ortho* to the ring nitrogens are more clearly separated. The multiplet at 8.91 ppm is assigned to the protons ortho to the Cr-coordinated nitrogen and that at 8.85 ppm assigned to those ortho to the Mo-

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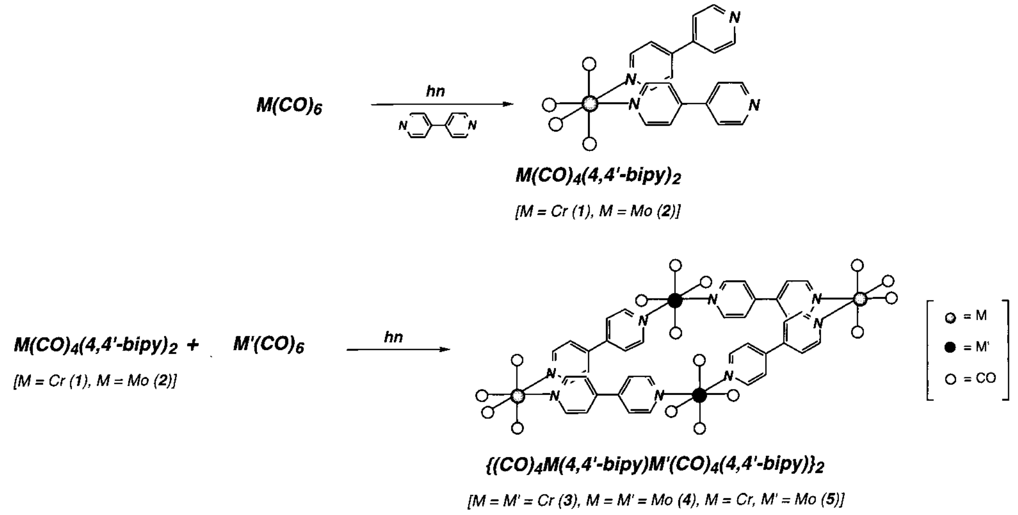
Scheme 1



coordinated nitrogen. In all cases, integration of the proton signals is consistent with the requirements for the molecular squares.

If **3**−**5** were acyclic oligomers, additional IR and NMR signals would be observed for even the simplest of stable cases, such as (4,4′-bipy)$M(CO)_4$(4,4′-bipy)$M(CO)_4$(4,4′-bipy)($M(CO)_4$-(4,4′-bipy) or $M(CO)_5$(4,4′-bipy)$M(CO)_4$(4,4′-bipy)$M(CO)_5$. Although formation of other cyclic oligomers such as a hexamer are permitted, the 90° N−M−N(cis) bond angles means that such molecules would have significant ring strain.

The electronic spectra of a range of heterocyclic derivatives of group 6 carbonyls have been studied and discussed previously.[14−17] The lowest energy transition in the electronic absorption spectra of **1** and **2** is substantially red shifted by formation of the square, consistent with the assignment of this feature as a metal-to-ligand charge-transfer transition (MLCT). In **1** and **2** the MLCT transitions are at 458 and 437 nm, respectively, whereas in **3**−**5** they are observed at 481, 468, and 472 nm, respectively. The fact that the transition moves significantly on formation of the square suggests that the energy of the π^*-acceptor orbitals on the 4,4′-bipy ligand are effectively lowered on association of the monomers to form a square. The peaks observed in **3**−**5** at between 395 and 415 nm are attributed to ligand field transitions. These are not shifted significantly from those observed in **1** and **2**. The $\pi-\pi^*$ ligand−ligand transitions of the 4,4′-bipy observed at ca. 245 nm in **1** and **2** are essentially unaffected by formation of the squares.

We have met with little success to date in our attempts to prepare the tungsten-containing square $\{W(CO)_4$(4,4′-bipy)$\}_4$. On photolysis, instead of cyclizing, the mixture of $W(CO)_4$-(4,4′-bipy)$_2$ and $W(CO)_6$ yielded side products which were tentatively assigned as polymers on the basis of mass spectroscopic data together with their insolubility in any common organic solvents. The exact composition of the polymers is as yet undetermined.

In an attempt to show the versatility and applicability of photochemistry to the synthesis of molecular squares, we have prepared one of the few previously reported organometallic square complexes $\{Re(CO)_3Cl$(4,4′-bipy)$\}_4$ (**6**) by this route. Using thermolysis, **6** is formed by heating a 3:1 tetrahydrofuran (thf)/toluene solution of $Re(CO)_5Cl$ and 4,4′-bipyridine at 60 °C for 36−48 h.[18] We have prepared **6** in 40 min by first generating the corner fragment $Re(CO)_3Cl$(4,4′-bipy)$_2$ photochemically and then reacting this with a stoichiometric equivalent of $Re(CO)_5Cl$, again photochemically.

In conclusion, photochemistry has been used as a synthetic method to prepare organometallic molecular square complexes. The potential and versatility of this work is exciting, and attempts are now being made to extend the area and prepare other supramolecular architectures.

Experimental Section

All syntheses were performed under an inert atmosphere of dry nitrogen. All photochemical reactions were performed in a specially designed glass reaction vessel fitted with a nitrogen bubbler and reflux condenser. A 125 W mercury arc broad-band UV immersion lamp was used as the irradiation source. Infrared (IR) spectra were recorded using a Perkin-Elmer PE 1710 Fourier transform infrared spectrometer, solution spectra in NaCl solution cells (path length 0.5 mm) and solid-state spectra in compressed KBr pellets. All values quoted are in wavenumbers (cm^{-1}). UV−vis spectra were recorded on a Perkin-Elmer 5523 UV−vis spectrophotometer stabilized at 20 °C. All values quoted are in nanometers. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded using a Bruker AM400, WM250, or WP80SY Fourier transform NMR spectrometer and data reported using the chemical shift scale in units of ppm relative to $SiMe_4$ ($\delta = 0$). Mass spectra were recorded using a Kratos MS-50 spectrometer, with either 3-nitrobenzyl alcohol or thioglycerol as a matrix and CsI as calibrant. All reagents were purchased from commercial sources and used as received unless noted otherwise.

1. A solution of $Cr(CO)_6$ (30 mg, 0.136 mmol) and 4,4-bipy (43 mg, 0.273 mmol) in dichloromethane (100 mL) was irradiated for 10 min, the reaction mixture being stirred and maintained at 10 °C. Removal of the solvent in vacuo and washing the residue with hexane several times removed any unreacted starting materials. IR, NMR, and mass spectroscopic analysis of the resultant deep maroon solid and comparison of the data with those reported in the literature[6] showed that the only product formed in the reaction was $Cr(CO)_4$(4,4′-bipy)$_2$, **1**, being recovered in 95% yield (62 mg, 0.1292 mmol): IR (CH_2Cl_2) $\nu_{CO} = 2006$ (m), 1888 (vs), 1877 (vs), 1837(s) cm^{-1}; UV/vis (CH_2Cl_2) $\lambda_{max} = 245$ ($\lambda_{\pi-\pi^*}$), 408 (λ_{LF}), 458 (λ_{MLCT}) nm; ^1H NMR (250 MHz, 25 °C, $CDCl_3$) $\delta = 8.85$ (d, 2H), 8.81 (d, 2H), 7.49 (d, 2H), 7.45 (d, 2H) ppm; $^{13}C\{^1H\}$ NMR (250 MHz, 25 °C, $CDCl_3$) 201.5, 156.0, 151.0, 145.9, 145.3, 122.3, 120.9 ppm; mass spectrum $m/z = 477$ (calcd 476).

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2. The method of preparation and purification was as for **1**, using Mo(CO)$_6$ (30 mg, 0.114 mmol) and 4,4′-bipy (36 mg, 0.227 mmol) again comparing spectroscopic data with literature values.[6] A 90% yield of deep maroon Mo(CO)$_4$(4,4′-bipy)$_2$, **2** (53 mg, 0.102 mmol), was obtained: IR (CH$_2$Cl$_2$) $\nu_{\mathrm{CO}} = 2013$ (m), 1895 (vs), 1879 (vs), 1835 (s) cm^{-1}; UV/vis (CH$_2$Cl$_2$) $\lambda_{\max} = 245(\lambda_{\pi-\pi^*})$, 391 ($\lambda_{\mathrm{LF}}$), 437 ($\lambda_{\mathrm{MLCT}}$) nm; ^{1}H NMR (250 MHz, 25 °C, CDCl$_3$) $\delta = 8.83$ (d, 2H), 8.79 (d, 2H), 7.53 (d, 2H), 7.48 (d, 2H) ppm; ^{13}C{^{1}H} NMR (250 MHz, 25 °C, CDCl$_3$) 203.2, 154.3, 151.0, 145.9, 145.3, 128.8, 122.5 ppm; mass spectrum $m/z = 519$ (calcd 520).

3. A solution of **1** (30 mg, 0.063 mmol) and Cr(CO)$_6$ (14 mg, 0.063 mmol) in dichloromethane (400 mL) was irradiated, the reaction mixture being stirred and maintained at 10 °C. IR monitoring of the reaction showed complete loss of the signals due to Cr(CO)$_6$ after 20 min. The irradiation was stopped at this point. Removal of the solvent in vacuo and washing the residue with cold hexane and then cold 5:1 hexane/dichloromethane several times removed any unreacted starting materials. The addition of dichloromethane to the resultant solid and subsequent removal of the deep purple solution was repeated several times until the dichloromethane was no longer colored on shaking with the remnant solid. Removal of the dichloromethane from the collected washings lead to the recovery of a deep maroon solid, characterized as **3** (56 mg, 0.044 mmol, 70% yield). IR and NMR analyses show that **3** is the only species present in solution as no other peaks are observed. The material must be handled under strictly anaerobic conditions and stored in the solid state in a refrigerator. IR (CH$_2$Cl$_2$) $\nu_{\mathrm{CO}} = 2006$ (m), 1887 (vs), 1881 (vs), 1838(s) cm^{-1}; UV/vis (CH$_2$Cl$_2$) $\lambda_{\max} = 245$ ($\lambda_{\pi-\pi^*}$), 413 (λ_{LF}), 481 (λ_{MLCT}) nm; ^{1}H NMR (250 MHz, 25 °C, CDCl$_3$) $\delta =$ 8.93 (d, 4H), 7.52 (d, 4H) ppm; ^{13}C{^{1}H} NMR (250 MHz, 25 °C, CDCl$_3$) 201.5, 156.2, 145.9, 122.3 ppm.

4. The method of synthesis and purification was as for **3**, using **2** (30 mg, 0.058 mmol) and Mo(CO)$_6$ (15 mg, 0.058 mmol). Very deep maroon **4** (64 mg, 0.044 mmol) was recovered in 75% yield. IR and NMR analyses show that **4** is the only species present in solution as no other peaks are observed: IR (CH$_2$Cl$_2$) $\nu_{\mathrm{CO}} = 2013$ (m), 1894 (vs), 1883 (vs), 1838 (s) cm^{-1}; UV/vis (CH$_2$Cl$_2$) $\lambda_{\max} = 245$ ($\lambda_{\pi-\pi^*}$), 395 (λ_{LF}), 468 (λ_{MLCT}) nm; ^{1}H NMR (250 MHz, 25 °C, CDCl$_3$) $\delta = 8.82$ (d, 4H), 7.71 (d, 4H) ppm; ^{13}C{^{1}H} NMR (250 MHz, 25 °C, CDCl$_3$) 203.3, 154.5, 150.0, 128.5 ppm; mass spectrum $m/z = 1457$ (calcd 1456). Anal. Calcd for $C_{56}H_{32}N_8O_{16}Mo_4$: C, 46.1; H, 2.2; N, 7.7. Found: C, 46.3; H, 2.3; N, 7.6.

5. The method of synthesis and purification was as for **3**, using **2** (30 mg, 0.058 mmol) and Cr(CO)$_6$ (13 mg, 0.058 mmol). Very deep maroon **5** (56 mg, 0.041 mmol) was recovered in 70% yield. IR and NMR analyses show that **5** is the only species present in solution as no other peaks are observed: IR (CH$_2$Cl$_2$) $\nu_{\mathrm{CO}} = 2012$ (m), 2008 (m), 1896 (vs), 1888 (vs), 1883 (vs), 1876 (vs), 1839 (s), 1830 (s) cm^{-1}; UV/vis (CH$_2$Cl$_2$) $\lambda_{\max} = 245$ ($\lambda_{\pi-\pi^*}$), 403 (λ_{LF}), 452 (λ_{MLCT}) nm; ^{1}H NMR (250 MHz, 25 °C, CDCl$_3$) $\delta = 8.91$ (d, 2H), 8.87 (d, 2H), 7.56 (d, 2H), 7.51 (d, 2H) ppm; ^{13}C{^{1}H} NMR (250 MHz, 25 °C, CDCl$_3$) 202.1, 203.5, 157.0, 155.4, 150.6, 146.2, 128.4, 121.4 ppm. IR (acetone, cm^{-1}) ν_{CO} 2024 (vs), 1923 (s), 1893 (d); ^{1}H NMR (acetone-d_6, ppm) 8.95 (d, 16H), 7.97 (d, 16H); mass spectrum $m/z = 1847$ (calcd 1848).

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