Luckham, S. L. J., Folli, A., Platts, J. A., Richards, E., & Murphy, D. M. (2019). Unravelling the Photochemical Transformations of Chromium(I) 1,3 Bis(diphenylphosphino), [Cr(CO)₄(dppp)]⁺, by EPR Spectroscopy. *Organometallics*. https://doi.org/10.1021/acs.organomet.9b00226
Unravelling the Photochemical Transformations of Chromium(I) 1,3 Bis(diphenylphosphino), [Cr(CO)₄(dppp)]⁺, by EPR Spectroscopy

Stephen L. J. Luckham, Andrea Folli, James A. Platts, Emma Richards, and Damien M. Murphy

School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, U.K.
School of Chemistry, University of Bristol, Cantock’s Close, Bristol BS8 1TS, U.K.

ABSTRACT: UV-induced photochemical transformations of the paramagnetic [Cr(CO)₄(Ph₂PCH₂CH₂CH₂PPh₂)]⁺ complex (abbreviated [Cr(CO)₄(dppp)]⁺) in dichloromethane was investigated by CW EPR spectroscopy. Room-temperature UV irradiation results in the rapid transformation of [Cr(CO)₄(dppp)]⁺ into trans-[Cr(CO)₄(Ph₂PN(PhPr))]. However, low-temperature (77−120 K) UV irradiation reveals the presence of an intermediate mer-[Cr(CO)₃(k⁺-dppp)(k²-dppp)]⁺ complex which photochemically transforms into trans-[Cr(CO)₄(Ph₂PN(PhPr))]. The derived spin Hamiltonian parameters for these complexes were confirmed by DFT calculations. The photoinduced reaction is shown to be concentration-dependent, leading to a distribution of the three complexes ([Cr(CO)₄(dppp)]⁺, mer-[Cr(CO)₃(k⁺-dppp)(k²-dppp)]⁺, and trans-[Cr(CO)₄(Ph₂PN(PhPr))]). A bimolecular photoinduced mechanism is proposed to account for the formation of mer-[Cr(CO)₃(k⁺-dppp)(k²-dppp)]⁺ and trans-[Cr(CO)₄(Ph₂PN(PhPr))].

INTRODUCTION

Cr-based complexes are important catalysts for the selective trimerization/tetramerization of ethylene to yield highly desirable linear α-olefins. These catalysts typically employ ligands based on bis(phosphino)amines and bis(sulfanyl)amines, whereby the activity and selectivity of the catalytic reactions can in principle be tuned by varying the nature of the ancillary ligands. Since the first reports of ethylene tetramerization toward 1-octene using chromium-bis(diphenylphosphino)amine (Cr-PNP) catalysts, many studies have focused on the mechanism, with particular reference to the oxidation states of the active chromium centers. In most cases, these Cr-based complexes are generally activated prior to catalysis by addition of an alkylaluminum cocatalyst, such as triethylaluminum (Et₃Al) or methylaluminoxane (MAO). While electron paramagnetic resonance (EPR) studies have been used to study the oxidation states of chromium following the activation step, previous work from our group revealed the important role that the ligand itself plays in adopting various conformations of the partially or fully decarbonylated complexes. For example, addition of triethylaluminum (Et₃Al) in nonaromatic solvents to [Cr(CO)₂(dppp)]⁻ (1,2-bis(diphenylphosphino)ethane, Ph₂P(C₂H₄)−PPh₂ = dpe) or [Cr(CO)₄(Ph₂PN(iPr)PPh₂)]⁻ (1,2-bis(diphenylphosphino)-isoproplylene, Ph₂PN(iPr)PPh₂) resulted in the formation of the Cr(I)-bis-η⁵-arene complex, formed via intramolecular rearrangement and coordination of Cr(1) to the phenyl groups of the bis(diphenylphosphino)ligand. Several additional complexes, including cis-[Cr(CO)₅(Ph₂PN(iPr)PPh₂)]⁻ and the piano-stool type [Cr(CO)₅(Ph₂PN(iPr)PPh₂)]⁻ complexes, were also identified following Et₃Al activation of [Cr(CO)₄(Ph₂PN(iPr)PPh₂)]⁻, revealing the structural rearrangements that occur in these complexes.

Despite the widely studied chemistry of these tetracarbonyl chromium-bis(diphenylphosphino)amine complexes, particularly from the perspective of catalysis, what remains sparsely studied to date is the photochemistry of these Cr(I) systems. The photochemistry, photophysics, and photoelectrochemistry of metal carbonyl complexes have, in general, been studied extensively over the years, and for example, the loss of a carbonyl ligand from Cr(CO)₆ is one of the fastest photochemically induced processes known, occurring on a femtosecond time scale. With respect to Cr(0) tetracarbonyl complexes, Perutz et al. performed very detailed transient absorption studies on the phototransformations of the (bis(bis(penta-fluoroethyl)phosphino)ethane) tetracarbonyl chromium complex. Photocactivity of Cr(I) complexes by UV was also observed by researchers at SASOL, using the same alkylaluminum cocatalyst as used here. Interestingly, they also observed (via IR) the reformation of the Cr(0) complexes.
complex following UV irradiation, accounting for the observed loss of Cr(I) centers. By comparison, the photochemistry of Cr(I) complexes with fac- and mer-[Cr(CO)4(κ²-L2)]+ (L2 = bidentate phosphine, abbreviated as dppe) coordination has been less widely investigated by EPR. The facial complex was shown to rapidly isomerize to the meridional structure via a thermally activated process. The mer-complex was then found to lose CO in a photochemical UV-driven trans-d + single-electron oxidation of the Cr(0) complexes were initially synthesized and isolated, before one-electron oxidation of the mer-complex by [Fe(η-C5H5)2]+ or [O2NC6H4N2]+ to give the corresponding Cr(I) species. To date, the photochemistry and UV-induced decarbonylation of the paramagnetic [Cr(CO)4(Ph2P(C3H6)PPh2)]+ (1,3 bis(diphenylphosphino)propane, Ph2P(C3H6)PPh2 = dppp), has never been investigated. Therefore, using EPR and DFT, herein we explore for the first time the photochemical transformations of the tetracarbonyl Cr(I) system, [Cr(CO)4(dppp)]+ (Scheme 1) and examine the underlying photoinduced mechanism.

Scheme 1. Structure of the Chromium(I) 1,3 Bis(diphenylphosphino) Complex Investigated Herein (Labeled [Cr(CO)4(dppp)]+) and the Associated Counterion

### RESULTS AND DISCUSSION

The 140 K CW EPR spectrum of [Cr(CO)4(dppp)]+ (compound 1) in frozen solution is shown in Figure 1a. This EPR spectrum, previously discussed in detail by us for a series of analogous Cr(I) complexes, is characterized by an axial g tensor (g∥ > g⊥ > gA) with a large hyperfine coupling characterized by a 1:2:1 multiplet pattern, originating from the interaction of the unpaired electron with two equivalent 31P (I = 1/2) nuclei (Table 1). The spin Hamiltonian parameters, obtained by simulation of the experimental spectra, were shown to be consistent with a low-spin d^5 Cr(I) center possessing a SOMO of largely d_σ character. The corresponding fluid solution (i.e., isotropic) EPR spectrum produces a broad, structureless signal due to fast relaxation characteristics. The simulated spin Hamiltonian parameters are in good agreement with the parameters obtained by DFT for the geometry optimized structure (Figure 2).

Following UV irradiation of the [Cr(CO)4(dppp)]+ complex at 298 K (after ca. 30 min), the intense blue coloration of the solution changed to pale yellow and this was accompanied by a significant change to the anisotropic EPR spectrum (Figure 1b). A new EPR spectrum can be identified by a characteristic axial g and 2A profile with g∥ = 2.024 and g⊥ = 1.968, possessing a notably smaller g anisotropy compared to the starting [Cr(CO)4(dppp)]+ complex (Table 1). Changes to the multiplicity of the 31P superhyperfine coupling, which is superimposed on both the parallel and perpendicular components of the signal, are also clearly observed. This indicates the formation of a new Cr(I) complex. The distinctive 5-line multiplet pattern (with relative intensities of 1:4:6:4:1) is more readily resolved in the isotropic EPR spectrum (Figure 1c) because of coupling of the unpaired electron with four equivalent 31P nuclei. At high resolution, weak 53Cr satellite features are also observed in the wings of this isotropic spectrum (see Figure S13), confirming the origin of the signal to a Cr(I) center. Simulation of the anisotropic and isotropic EPR spectra for this new complex revealed the 2A coupling components to be a_σ = –81.3 MHz, A_∥ = –82 MHz, and A_⊥ = –80 MHz. The negative sign of the superhyperfine couplings is chosen to be compatible with the DFT-calculated values, which predict a negative spin density at the phosphorus atom. There is indeed negative spin density on the P atoms: Mulliken spin density on coordinated P is consistently around ~0.03 to ~0.04 e. We attribute this to mixing of metal d-orbitals with ligand-based ones in the less-than-octahedral symmetry of these complexes, which is also evident in Mayer bond orders for Cr–P of 0.5. The 31P superhyperfine tensor orientations (and matrices) are shown in the SI, along with a summary table of the spin Hamiltonian parameters for a general series of Cr(I) complexes.

The new Cr(I) complex identified in Figure 1b,c must arise from a partially decarbonylated complex in which two equivalents of the dppp ligand are now directly coordinated to the chromium metal center in a trans- conformation, hereafter labeled trans-[Cr(CO)4(dppp)]+ (compound 2). The spin Hamiltonian parameters for this trans-[Cr(CO)4(dppp)]+ complex, obtained by simulation of the spectra, are in good agreement with the DFT derived values.
Table 1. Spin Hamiltonian Parameters for the Three Paramagnetic Cr(I) Complexes, \([\text{Cr(CO)}_4(\text{dppp})^+\) (1), trans-\([\text{Cr(CO)}_2(\text{dppp})_2]^+\) (2) and mer-\([\text{Cr(CO)}_3(\kappa^1-\text{dppp})(\kappa^2-\text{dppp})]^+\) (3)\(^a\)

| compound | \(g_1\) | \(g_2\) | \(g_3\) | \(\alpha\) /deg | \(\beta\) /deg | \(\gamma\) /deg | \(A_{1}\) /MHz | \(A_{2}\) /MHz | \(A_{3}\) /MHz | \(\alpha\) Euler angles rotation of the A frame with respect to the molecular frame |
|-----------|--------|--------|--------|----------------|----------------|----------------|----------------|----------------|----------------|--------------------------------------------------|
| \(1\) expt | 1.988  | 2.066  | 2.066  | –180          | 90             | 60             | –65            | –77            | –77            | –120 160 120 |
| DFT       | 1.992  | 2.029  | 2.039  | –188          | 99             | 66             | –68            | –70            | –78            | –115 156 110 |
| \(2\) expt | 1.968  | 2.024  | 2.024  | 90            | 120            | 180            | –80            | –82            | –82            | –20 120 45    |
| DFT       | 1.964  | 2.009  | 2.012  | 90            | 117            | 180            | –80            | –81            | –92            | –23 125 41    |
| \(3\) expt | 1.984  | 2.026  | 2.050  | 15            | 60             | 180            | –64            | –50            | –60            | –120 90 60    |
| DFT       | 1.982  | 2.014  | 2.024  | 14            | 64             | 172            | –43            | –47            | –60            | –120 85 68    |

\(^a\)Uncertainties of the experimental spin Hamiltonian parameters are \(\pm 0.003\) for the \(g\)-values and \(\pm 3\) MHz for the super-hyperfine couplings. Euler angles are provided in degrees with uncertainties of \(\pm 10\) deg. In the mer-\([\text{Cr(CO)}_3(\kappa^1-\text{dppp})(\kappa^2-\text{dppp})]^+\) (3) complex, the theoretical hyperfine couplings to the second \(31P\) on the \(\kappa^4\)-dppp ligand, which is not directly binding to the Cr center, are shown in italics and they could not be measured experimentally by CW EPR (vide infra).

(Table 1). The observed parameters are also analogous to those previously reported in the literature for structurally similar complexes, but in those cases, the complexes were typically formed via chemical or electrochemical oxidation of the \(\text{Cr}(0)\) mer-\([\text{Cr(CO)}_2(\kappa^1-\text{L}_2)(\kappa^2-\text{L}_2)]^0\) (\(\text{L}_2 = \) bidentate phosphine) structures yielding the paramagnetic Cr(I) system which then slowly decays to the trans-\([\text{Cr(CO)}_2(\text{L}_2)_2]^+\) complex (Table 1). In the current work, the EPR spectrum of trans-\([\text{Cr(CO)}_2(\text{dppp})_2]^+\) (Figure 1b,c) remained unchanged following storage in the dark at 298 K for 48 h, indicating that this complex is kinetically inert. The equivalence of the \(31P\) hyperfine couplings in the spectra (Figure 1b,c) also clearly indicate the formation of the trans-isomer, as opposed to the cis-isomer, in agreement with the known preference for stabilization of trans-complexes over the corresponding cis-Cr(I) complexes.\(^22\)

Formation of the trans-\([\text{Cr(CO)}_2(\text{dppp})_2]^+\) complex, starting only from \([\text{Cr(CO)}_4(\text{dppp})]^+\), clearly requires the presence of two dppp ligands for every Cr(I) center. Considering no excess ligand was present in the studied system, this implies that 2 equiv of the starting \([\text{Cr(CO)}_4(\text{dppp})]^+\) complex are required for formation of 1 equiv of trans-\([\text{Cr(CO)}_2(\text{dppp})_2]^+\). Interestingly, the formation of trans-\([\text{Cr(CO)}_2(\text{dppp})_2]^+\) (Figure 1b) is accompanied by a considerable loss of EPR signal intensity. One possible explanation is that \([\text{Cr(CO)}_3]^+\) is formed during the photochemical transformation of \([\text{Cr(CO)}_4(\text{dppp})]^+\) into trans-\([\text{Cr(CO)}_2(\text{dppp})_2]^+\) or that phosphine-free Cr(I) ions are released into solution and not observed by EPR. Although the EPR spectrum of \([\text{Cr(CO)}_3]^+\) has only once been reportedly observed at 4 K,\(^23\) Bond et al. gave a very comprehensive explanation on the failure to observe isotropic EPR signals for such a species.\(^24\) Therefore, if \([\text{Cr(CO)}_3]^+\) is indeed formed, it would prove exceedingly difficult to detect by conventional X-band EPR. All attempts to detect \([\text{Cr(CO)}_3]^+\) in our experiments by EPR, and additionally by chemical oxidation of \([\text{Cr(CO)}_6]^+\) with \(\text{Ag}[\text{OC(CF}_3)_2]_2\)\(^25\), proved to be unsuccessful, even at low temperatures (5 K). However, there is previous EPR evidence for this \(17e^-\) complex which was described as having a single broad line,\(^23\) while Pickett and Pletcher\(^26\) noted that disproportionation of the cation can occur yielding an unstable \([\text{Cr(CO)}_6]^+\) complex and reformation of the starting \([\text{Cr(CO)}_6]^+\). Evidence for the release of phosphine-free Cr(I) into solution was also explored here through the addition of toluene to the solvent mixture. In previous work by our group, chemical activation of \([\text{Cr(CO)}_4(\text{dppp})]^+\) resulted in the formation of a bis-toluene complex \([\text{Cr}(\eta^5-(\text{CH}_3)\text{C}_6\text{H}_5)_2]^+\) in aromatic solvents.\(^9,10\) Therefore, if free Cr(I) ions were released during the UV irradiation, it might reasonably be expected that a signal for \([\text{Cr}(\eta^5-(\text{CH}_3)\text{C}_6\text{H}_5)_2]^+\) could be detected; however no evidence for this signal was observed following UV irradiation in the presence of toluene.

To better understand the mechanism of trans-\([\text{Cr(CO)}_2(\text{dppp})_2]^+\) formation, the UV photolysis experiments of \([\text{Cr(CO)}_4(\text{dppp})]^+\) were conducted at low temperatures (77 K). A typical EPR spectrum obtained under these low-temperature conditions is shown in Figure 1d. UV irradiation at 77 K for up to 120 min led to a marked color change in the solution, from intense blue to green, resulting in the accompanying new signal shown in Figure 1d. Despite the broad line widths, it can clearly be seen that the profile of this
distinct sets of $^{31}$P couplings; one arising from a coupling to from those observed previously, owing to the presence of two (Figure 1d) could only be reproduced by including the complex. A satisfactory simulation of the EPR spectrum presumably owing to the fast relaxation behavior of the new solution. No room-temperature signal could be observed, suggesting a progressive loss of the EPR observable Cr(I) in (Figure 1d) decreased with increasing irradiation time, signal intensity of the low-temperature irradiated spectrum [Cr(CO)$_4$(dppp)]$^+$ complex (40% spectral contribution after 30 min of irradiation). The second center (60% spectral contribution after 30 min of irradiation) was however di...30 min of irradiation). The second center (60% spectral contribution after 30 min of irradiation) was however dis...the arbitrary molecular frame chosen (M$^x$, M$^y$, M$^z$) and with the g tensor principal axes in molecular frame coordinates (g$^x$, g$^y$, g$^z$).

Figure 2. Geometry-optimized structures of the paramagnetic Cr(I) complexes at the uBP86/def2-TZVP level of theory. Structures include (a) [Cr(CO)$_4$(Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$)]$^+$ (1) abbreviated as cis-[Cr(CO)$_4$(dppp)]$^+$, (b) trans-[Cr(CO)$_4$(dppp)]$^+$ (2), and (c) mer-[Cr(CO)$_4$(κ$^3$-dppp)(κ$^2$-dppp)]$^+$ (3). Each structure is depicted with the arbitrary molecular frame chosen (M$^x$, M$^y$, M$^z$) and with the g tensor principal axes in molecular frame coordinates (g$^x$, g$^y$, g$^z$).

The second larger $^{31}$P coupling (with $a_{iso} = -74.3$ MHz) then arises from the second $^{31}$P nucleus of this κ$^2$-bonded dppp ligand. One may have expected the two phosphorus nuclei from the κ$^2$-dppp bonded ligand to be magnetically equivalent, but this does not appear to be the case. The second $^{31}$P nucleus on the κ$^1$-dppp ligand, which is not directly binding to the Cr center, does not show any experimentally observable superhyperfine coupling, confirmed by the DFT A value and almost exactly zero spin density for this phosphorus atom.

This is the first observation of a photochemically formed mer-[Cr(CO)$_3$(κ$^1$-dppp)(κ$^2$-dppp)]$^+$ complex, although previous work demonstrated that the 17-electron mer-[Cr(CO)$_3$(κ$^1$-L$_2$)(κ$^2$-L$_2$)]$^+$ is the only carbonyl-containing species observed on the electrochemical time scale following electrochemical oxidation of mer-[Cr(CO)$_3$(κ$^1$-L$_2$)(κ$^2$-L$_2$)].$^{19−22}$ The monodentate (κ$^2$-dppp) ligand may alter its coordination role more readily than the bidentate analogues,$^{20}$ and therefore, the choice of backbone linker chain length is expected to be extremely important in determining the thermodynamic and kinetic stability of the 17-electron complexes. It is also known that the facial (fac-) complexes rapidly isomerize to meridional (mer-) ones by a thermally activated process,$^{22}$ so one would not expect to see the fac- complex by EPR.

The EPR spectra obtained upon UV irradiation at 77 K were double integrated, and the values of the 2-fold integrals were plotted vs irradiation time, $t_{irr}$ (Figure 3). In the best-case scenario of the bimolecular reaction going to completion, one

Characterized by $A_\perp = −70$ to $−83$ MHz and $A_\parallel = −70$ MHz ($a_{iso} = −74.3$ MHz). It should be recalled that in [Cr(CO)$_4$(dppp)], the two $^{31}$P nuclei are equivalent, while in trans-[Cr(CO)$_4$(dppp)], all four $^{31}$P nuclei are equivalent.

The new Cr(I) species responsible for Figure 1d and formed by low-temperature UV irradiation, can be assigned to the meridional (mer-) [Cr(CO)$_3$(κ$^1$-dppp)(κ$^2$-dppp)]$^+$ complex (compound 3, shown in Figure 2c). In this complex, one dppp ligand coordinates in a bidentate mode, while the second ligand coordinates in a monodentate mode. According to DFT, the two magnetically equivalent $^{31}$P nuclei arise from one $^{31}$P nucleus on the κ$^1$-dppp ligand and one $^{31}$P on the κ$^2$-dppp bonded ligand, in trans-position with respect to each other. The second larger $^{31}$P coupling (with $a_{iso} = −74.3$ MHz) then arises from the second $^{31}$P nucleus of this κ$^2$-bonded dppp ligand. One may have expected the two phosphorus nuclei from the κ$^2$-dppp bonded ligand to be magnetically equivalent, but this does not appear to be the case. The second $^{31}$P nucleus on the κ$^1$-dppp ligand, which is not directly binding to the Cr center, does not show any experimentally observable superhyperfine coupling, confirmed by the DFT A value and almost exactly zero spin density for this phosphorus atom.

This is the first observation of a photochemically formed mer-[Cr(CO)$_3$(κ$^1$-dppp)(κ$^2$-dppp)]$^+$ complex, although previous work demonstrated that the 17-electron mer-[Cr(CO)$_3$(κ$^1$-L$_2$)(κ$^2$-L$_2$)]$^+$ is the only carbonyl-containing species observed on the electrochemical time scale following electrochemical oxidation of mer-[Cr(CO)$_3$(κ$^1$-L$_2$)(κ$^2$-L$_2$)].$^{19−22}$ The monodentate (κ$^2$-dppp) ligand may alter its coordination role more readily than the bidentate analogues,$^{20}$ and therefore, the choice of backbone linker chain length is expected to be extremely important in determining the thermodynamic and kinetic stability of the 17-electron complexes. It is also known that the facial (fac-) complexes rapidly isomerize to meridional (mer-) ones by a thermally activated process,$^{22}$ so one would not expect to see the fac- complex by EPR.

The EPR spectra obtained upon UV irradiation at 77 K were double integrated, and the values of the 2-fold integrals were plotted vs irradiation time, $t_{irr}$ (Figure 3). In the best-case scenario of the bimolecular reaction going to completion, one

![Figure 3. Kinetics of the transformation of starting [Cr(CO)$_4$(dppp)]$^+$ into mer-[Cr(CO)$_3$(κ$^1$-dppp)(κ$^2$-dppp)]$^+$ following UV irradiation at 77 K.](Image 2526)
Scheme 2. Proposed Mechanism for Photoinduced Formation of trans-[Cr(CO)2(dppp)2]+

Pathway 1: Initial dissociation of CO

Pathway 2: Initial dissociation of P

would expect a total loss of spins equal to 50%, if donation of a dppp ligand from one molecule of starting complex to another one results in the former becoming EPR silent (see above). Nevertheless, the trend observed does not asymptotically approach 0.5 but a much lower value, 0.0945. This might indicate that during molecular scrambling leading to the formation of the mer-intermediate, the activated complexes of the reaction pathway (Scheme 2) could also lead to the formation of EPR silent byproducts, where disproportionation of two Cr(I) centers might be envisaged, in line with the observations by Rucklidge et al. \(^\text{16}\)

Furthermore, in contrast to trans-[Cr(CO)2(dppp)2]+, the photochemically formed mer-[Cr(CO)3(κ^1-dppp)(κ^2-dppp)]+ was found to be unstable. When it was allowed to stand in the dark at 298 K for 3 h after irradiation, the mixture of starting and mer-complexes revealed the presence of starting [Cr(CO)3(dppp)] complex only, with, as expected, considerably lower signal intensity and depending on the concentration of the starting solution. Previous EPR studies demonstrated the slow transformation of the electrochemically generated mer-[Cr(CO)3(κ^1-dppm)(κ^2-dppm)] into the trans-[Cr(CO)3(κ^1-dppm)] complex. \(^\text{18}\) However, it may be assumed that depending on the solution concentration, it is possible for photochemically generated mer-[Cr(CO)3(κ^1-dppp)(κ^2-dppp)]+ to transform back to [Cr(CO)3(dppp)]+. Riegler also reported that the formation of the trans-Cr(I) complex from the mer-complex is a clean and highly efficient process. \(^\text{17}\)

In a series of [Cr^0(CO)4(L2)] complexes (where L2 = dppm, dppe, dppp), both the Cr—CO and Cr—P bonds are photolabile. \(^\text{15}\) It is therefore not unreasonable to suggest that the same competitive dissociation may be occurring within the Cr(I) complex investigated here. At suitable concentrations, an intramolecular exchange of P and CO ligands could occur (analogous to the Cr^0(CO)4 photochemistry) between neighboring Cr(I) complexes leading to a scrambling of the ligands (Scheme 2). Transient bridged Cr(PPP)-Cr dimers can then conceivably form, resulting in the eventual exchange of one dppp ligand from one Cr center to a nearby Cr center, already bearing a κ^2-coordinated dppp ligand. This can then lead to the formation of the EPR visible mer-complex. To examine this, the photochemical experiments were repeated on solutions of [Cr(CO)3(dppp)] at three different concentrations. At the highest and lowest concentrations respectively studied here (19.4 and 1.62 mM), no mer-[Cr(CO)3(κ^1-dppp)(κ^2-dppp)]+ (Figure 1d) or trans-[Cr(CO)3(dppp)2]+ (Figure 1b,c) complexes were visible in the EPR spectra. At intermediate concentrations (9.7 mM; Figure 1), the mer-[Cr(CO)3(κ^1-dppp)(κ^2-dppp)]+ and trans-[Cr(CO)3(dppp)2]+ complexes were readily observed. These results confirm the importance of the concentration-dependent biomolecular mechanisms proposed in Scheme 2. At the highest concentrations (19.4 mM), the intramolecular exchange may reversibly and competitively lead to formation of the starting complex or other EPR silent species, since the overall Cr(I) signal intensity decreased with irradiation time (showing a progressive loss of [Cr(CO)3(dppp)]+). At the lowest concentrations (1.62 mM), formation of the bridged Cr-dppp-Cr dimers appear to be inhibited, possibly because of an increase of the mean free path, as no mer-[Cr(CO)3(κ^1-dppp)(κ^2-dppp)]+ complex was found under these conditions.

CONCLUSIONS

A combined CW EPR spectroscopy and DFT computational study of a Cr(I)bis(phosphine) complex has been performed to investigate the decarbonylation and phototransformation process of the complex following UV irradiation. Room-temperature irradiation results in the loss of two CO ligands and coordination of an additional dppp phosphine ligand in a bimolecular reaction that produces the stable trans-[Cr(CO)3(dppp)]+ complex. On the other hand, low-temperature irradiation (77 K) results in partial loss of CO and formation of the intermediate mer-[Cr(CO)3(κ^1-dppp)(κ^2-dppp)]+ complex. Upon further UV irradiation at 298 K, this mer-species can undergo intramolecular CO displacement to form the stable trans-[Cr(CO)3(dppp)]+ complex. The spin Hamiltonian parameters characterizing the mer-[Cr(CO)3(κ^1-dppp)(κ^2-dppp)]+ and trans-[Cr(CO)3(dppp)2]+ complexes...
were obtained by simulation of the EPR spectra and confirmed by DFT calculations. The photoinduced formation of the trans-[Cr(CO)4(dppp)]+ complex was shown to be concentration-dependent, indicative of a bimolecular mechanism involving two [Cr(CO)4(dppp)]+ complexes. While these results demonstrate that the [Cr(CO)4(dppp)]+ complex can undergo facile photoinduced decarbonylation, clear similarities exist with the analogous Cr(0) photochemistry, and this opens up the possibility of generating chromium alkene carbonyl complexes.

**EXPERIMENTAL SECTION**

All manipulations were performed under a dry and inert atmosphere (N₂ or Ar) using standard Schlenk-line and glovebox techniques. Anhydrous solvents were obtained using an Anhydrous Engineering double alumina column drying system. CDCl₃ was degassed and dried over activated molecular sieves (4 Å). 1,1,1,3,3-pentafluorobenzene-propane (dppp) and silver tetrakis (perfluoro-tert-butoxy)aluminate (Ag[Al(OC(CF₃)₃)₄]) were purchased from Sigma and Iolitec, respectively, and used as received. Cr(CO)₄(dppp) and [Cr(CO)₂(dppp)₂]+ complexes. While these exist with the analogous Cr(0) photochemistry, and this opens up the possibility of generating chromium alkene carbonyl complexes.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00226.

- Orientations of the g and A tensors exemplified for the case of the starting [Cr(CO)₄(dppp)]⁺ (1) complex; high-resolution room-temperature spectrum of trans-[Cr(CO)₂(dppp)₂]+ (2) showing satellite resonances arising from hyperfine coupling to the ⁵³Cr nucleus; and spin Hamiltonian parameters of Cr(I) complexes similar to the ones described in the present work (PDF)
- Cartesian coordinates of the cis-[Cr(CO)₄(dppp)]⁺ geometry optimized structure (XYZ)
- Cartesian coordinates of the trans-[Cr(CO)₃(dppp)]⁺ geometry optimized structure (XYZ)
- Cartesian coordinates of the mer-[Cr(CO)₃(x⁻³-dppp)]⁻ geometry optimized structure (XYZ)

**AUTHOR INFORMATION**

**Corresponding Authors**

E-mail: follia@cardiff.ac.uk.
E-mail: richardse10@cardiff.ac.uk.
E-mail: murphydm@cardiff.ac.uk.

**ORCID**

Stephen L. J. Luckham: 0000-0003-3732-0668
Andrea Follì: 0000-0001-8913-6606
James A. Platts: 0000-0002-1088-6595
Damien M. Murphy: 0000-0002-3941-4879

**Notes**

The authors declare no competing financial interest.

Information on the data underpinning the results presented here, including how to access them, can be found in the Cardiff University data catalogue at http://doi.org/10.17035/d.2019.0077527126.

**ACKNOWLEDGMENTS**

EPSRC funding (EP/H023879, EP/P019951) is gratefully acknowledged. S.L.J.L. also acknowledges support from the EPSRC Centre for Doctoral Training in Catalysis (EP/L016443).

**REFERENCES**

(1) Rucklidge, A. J.; McGuinness, D. S.; Tooze, R. P.; Slavin, A. M. Z.; Pelletier, J. D. A.; Hanton, M. J.; Webb, P. B. Ethylene
Tetramerization with Cationic Chromium(1) Complexes. Organometallics 2007, 26, 2782.

(2) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Morgan, D.; Dixon, J. T.; Bollmann, A.; Maumela, H.; Hess, F.; Englert, U. First Cr(III)−SNS Complexes and Their Use as Highly Efficient Catalysts for the Trimerization of Ethylene to 1-Hexene. J. Am. Chem. Soc. 2003, 125, 5272.

(3) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. Advances in Selective Ethylene Trimerization—A Critical Overview. J. Organomet. Chem. 2004, 689, 3641–3668.

(4) McGuinness, D. S. Olefin Oligomerization via Metallacycles: Dimerization, Trimerization, Tetramerization, and Beyond. Chem. Rev. 2011, 111, 2321–2341.

(5) Radcliffe, E. J.; Batsanov, A. S.; Smith, D. M.; Scott, J. A.; Dyer, P. W.; Hanton, M. J. Phosphanyl Methanimine (PCN) Ligands for the Selective Trimerization/Tetramerization of Ethylene with Chromium. ACS Catal. 2015, 5, 7095–7098.

(6) Skobele, I. Y.; Panchenko, V. N.; Lyskin, O. Y.; Bryliakov, K. P.; Zakhvor, V. A.; Talsi, E. P. In Situ EPR Monitoring of Chromium Species Formed during Cr–Pyrryl Ethylene Trimerization Catalyst Formation. Organometallics 2010, 29, 2943–2950.

(7) Brückner, A.; Jabor, J. K.; McConnell, A. E.; Webb, P. B. Monitoring Structure and Valence State of Chromium Sites during Catalyst Formation and Ethylene Oligomerization by In Situ EPR Spectroscopy. Organometallics 2008, 27, 3849–3856.

(8) McDiyre, L. E.; Hamilton, T.; Murphy, D. M.; Cavell, K. J.; Gabrielli, W. F.; Hanton, M. J.; Smith, D. M. A cw EPR and ENDOR investigation on a series of Cr(I) carbonyl complexes with relevance to alkene oligomerization catalysis: [Cr(CO)4(L)−]− (L = Ph,P(R)=PPh2, Ph,P(R,R)=PPh2). Dalton Trans. 2010, 39, 7792–7799.

(9) McDiyre, L.; Carter, E.; Cavell, K. J.; Murphy, D. M.; Platts, J. A.; Sampford, K.; Ward, B. D.; Gabrielli, W. F.; Hanton, M. J.; Smith, D. M. Intramolecular Formation of a CrI(bis-arene) Species via TEA Activation of [Cr(CO)2(Ph,P(η3-C3H3)=PPh2)]−: An EPR and DFT Investigation. Organometallics 2011, 30, 4505–4508.

(10) Carter, E.; Cavell, K. J.; Gabrielli, W. F.; Hanton, M. J.; Hallett, A. J.; McDiyre, L. E.; Platts, J. A.; Smith, D. M.; Murphy, D. M. Formation of [Cr(CO)(Ph,P(η3-C3H3)=PPh2)] Structural Isomers by Reaction of Triethylaluminium with a Chromium N,N-Bis-dipyridylphosphine)amine Complex [Cr(CO)(Ph,P(η3-C3H3)=PPh2)]+: An EPR and DFT Investigation. Organometallics 2013, 32, 1924–1931.

(11) Mingos, D. M. P. The Electronic Factors Governing the Relative Stabilities of Geometric Isomers of Octahedral Complexes with π-acceptor and π-donor Ligands. J. Organomet. Chem. 1979, 179, C29–C33.

(12) Compton, R. G.; Barghout, R.; Eklund, J. C.; Fisher, A. C.; Davies, S. G.; Metzler, M. R.; Bond, A. M.; Colton, R.; Walter, J. N. Photoelectrochemistry of some organochromium carbonyl com-

(13) Szymanska-Buzar, T. Photochemical reactions of Group 6 metal carbonyls with alkenes. Coord. Chem. Rev. 2006, 250, 976–990.

(14) Gutmann, M.; Jamello, J. M.; Dickelbohm, M. S.; Groossekatheo, M.; Lindener-Roenneke, U. Ultrafast Dynamics of Transition Metal Carbonyls: Photodissociation of Cr(CO)5 and Cr(CO)5=CH2, Heterocycles at 280 nm. J. Phys. Chem. A 1998, 102, 4138–4147.

(15) Brookhart, M.; Chandler, W.; Kessler, R. J.; Liu, Y.; Pienta, N. J.; Santini, C. C.; Hall, C.; Perutz, R. N.; Timney, J. A. Matrix isolation and transient absorption studies of [bis[bis[pentafluoroethyl]-phosphino]ethane]tetracarbonylicromium: Intermolecular alkane complexes and intramolecular F-coordination. J. Am. Chem. Soc. 1992, 114, 3802–3815.

(16) Rucklidge, A. J.; McGuinness, D. S.; Toote, R. P.; Slawin, A. M. Z.; Pelletier, J. D. A.; Hanton, M. J.; Webb, P. B. Ethylene Tetramerization with Cationic Chromium(1) Complexes. Organometallics 2007, 26, 2782–2787.

(17) Rieger, A. L.; Rieger, P. H. EPR Study of Photochemical Reactions of fac- and mer-[Cr(CO)5(L−)](η2−L−) and trans-[Cr(CO)5(L−)](η2−L−) (L− = Bidentate Phosphine, Arsinie, or Phosphonite Ligand). Organometallics 2002, 21, 5868–5873.