



Synthesis and structure of three dichromium hexacarbonyl complexes with $(\text{CPh}_2)_2$, $(\text{CHPh}_2)_2$, and carbazole bridges

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ABSTRACT

Three dichromium hexacarbonyl complexes containing $(\text{CPh}_2)_2$, $(\text{CHPh}_2)_2$, and carbazole as a conjugated bridging ligand are synthesized and exhibit a variety of electronic interactions between the metal centers, which can be modified by altering either the conjugated bridging nature or the ligand bound to the metals to induce peculiar asymmetry.

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1. Introduction

There are increasing interests in the design of complexes in which two or more metal centers are simultaneously coordinated to a bridging ligand due to the possibility of a variety of indirect electronic interactions between metal units.¹ This type of novel multinuclei can be employed as models for organometallic polymers.² Chromium tricarbonyl species have shown to be ‘amphoteric’ for their ability to stabilize both benzylic cations and anions³ and exhibit an enhancement of reactivity through cooperative metal effects.⁴ Furthermore, the Cr atom in the involved complexes might be tuned to the expected state by substituting the auxiliary ligands for one or more of the carbonyls,⁵ for example, the electron-rich phosphine ligand⁶ bound to the metal provides a somewhat asymmetric environment, which plays a significant role in charge-transfer properties.⁷ Several reports mention bimetallic complexes with a hydrocarbon chain bonded to two aromatic rings of chromiumcarbonyl arene units.⁸ However, phosphine containing unsaturated carbon-rich bridges bonded to the two Cr atoms of chromiumcarbonyl arene units are not available in the literature. Recently, we synthesized a series of dichromium complexes with carbazole ligands bond to two $\text{Cr}(\text{CO})_3$ moieties,⁹ and thus the

metal centers interact strongly via the carbazole π -system. This intriguing characteristics greatly stabilizes the incorporated structure and enhances their nonlinear optical activity as well.^{9b} We present herein three new dichromium complexes with carbazole bridge **4**, $(\text{CPh}_2)_2$ **5** and $(\text{CHPh}_2)_2$ **6**. The sensitivity of electronic communications between the metal centers is proposed to be associated with the nature of the conjugated bridges or the ancillary ligand bound to the metals.

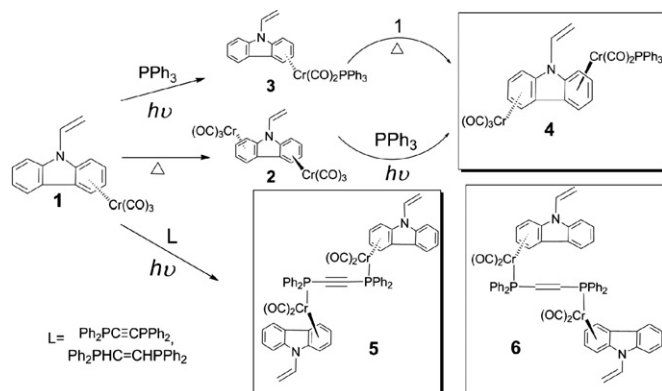
2. Results and discussion

2.1. Synthesis and crystal structures

The requisite complexes **1–3**^{9a} were readily prepared as reported. A carbazole-mediated metal–metal interaction makes **2** to have a very acentric electron distribution, profoundly affecting the reactivity of the *N*-vinyl group.^{9c} The photochemical activation of **2** with 2 equiv of PPh_3 in benzene under nitrogen atmosphere gave the asymmetric complex **4** (Scheme 1).^{9c} Notably, treatment of **4** with an excess of PPh_3 failed to form the dichromium complexes with two or more phosphine ligands, implying the high stability of complex **4**. Heating equal amounts of **1** and **3** in degassed dioxane at 65 °C for a predetermined period of time gives rise to conversion to **4** without formation of the analogous symmetric complexes with formula $(N\text{-vinylcarbazole})[\text{Cr}(\text{CO})_2\text{R}]_2$, where $\text{R}=\text{CO}$, PPh_3 .^{9a,10}

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Accumulation of stoichiometric amounts of **4** in the system refers to an efficient $\text{Cr}(\text{CO})_3$ and/or $\text{Cr}(\text{CO})_2\text{PPh}_3$ migration from one carbazole to the other to form the more stable complex. Clearly this dichromium complex does not behave like two separate metal units; the accepting $\text{Cr}(\text{CO})_3$ and donating $\text{Cr}(\text{CO})_2\text{PPh}_3$ within the same molecule interact strongly via the carbazole π -system, greatly stabilizing the asymmetric form of **4**. The NMR spectroscopic data of **4** are consistent with the assigned structure, and the EI-MS result shows a peak of the highest mass at $[\text{M}^+ - 2\text{CO}]$. Infrared spectroscopy reveals three Cr–CO bands centered at $\nu_{\text{CO}} = 1952, 1867, 1825 \text{ cm}^{-1}$, assuming the overlap of the ν_{sym} and ν_{asym} features for the two metal units.



Reactions of **1** with $(\text{CPhPh}_2)_2$ and $(\text{CHPhPh}_2)_2$ yielded **5** and **6**, respectively, as deep violet solids (Scheme 1). No traces of the mononuclear analogues $(N\text{-vinylcarbazole})\text{Cr}(\text{CO})_2\text{L}$ [$\text{L} = (\text{CPhPh}_2)_2, (\text{CHPhPh}_2)_2$] have been found in this reaction. Apparently a synergistic metal–metal interaction through the phosphine bridging ligands is essential for stabilizing the organometallic architecture. The analogous reaction of **2** with $(\text{CPhPh}_2)_2$ and $(\text{CHPhPh}_2)_2$ did not afford the desired complexes such as $[\text{Cr}(\text{CO})_3(N\text{-vinylcarbazole})\text{Cr}(\text{CO})_2]_n\text{L}$, where $n = 1, 2$ and $\text{L} = (\text{CPhPh}_2)_2, (\text{CHPhPh}_2)_2$. A very strong carbazole-mediated metal–metal interaction probably interrupted the metal–metal interaction through other bridging ligands in this case. The NMR data and mass spectrometry are consistent with the proposed structure of **5** and **6**. The infrared spectra of both complexes in the carbonyl stretching region are very different—three bands are seen in **5** ($\nu_{\text{CO}} = 1950, 1870, 1820 \text{ cm}^{-1}$), while **6** has two bands ($\nu_{\text{CO}} = 1952, 1853 \text{ cm}^{-1}$).¹¹ Compared with **5**, **6** may possess more conformers due to the very small rotational barrier for $\text{C}=\text{C}$ bond and, hence, the 1853 cm^{-1} band is rather broad and essentially an average of the 1870 and 1820 cm^{-1} bands. The change in Cr–CO frequencies prompts consideration of intramolecular metal–metal interaction and would be expected to show bridging ligand effects.

Crystals of **4** and **5** with acceptable quality were obtained from dichloromethane/pentane mixture at $-30 \text{ }^\circ\text{C}$. Views of one molecular of **4** and **5** are shown in Fig. 1 along with some important structural parameters. Complex **4** crystallizes together with one dichloromethane molecule per complex. The two chromium units are situated *anti* with respect to the carbazole plane. The chromium–arene distances are 1.724 and 1.736 \AA , indicating a stronger coordination occurred in the $\text{Cr}(\text{CO})_2\text{PPh}_3$ compared with the $\text{Cr}(\text{CO})_3$, even though the position of $\text{Cr}(\text{CO})_2\text{PPh}_3$ with respects to the phenyl ring is slightly distorted toward the four unsubstituted carbon atoms of the arene ring, resulting from the

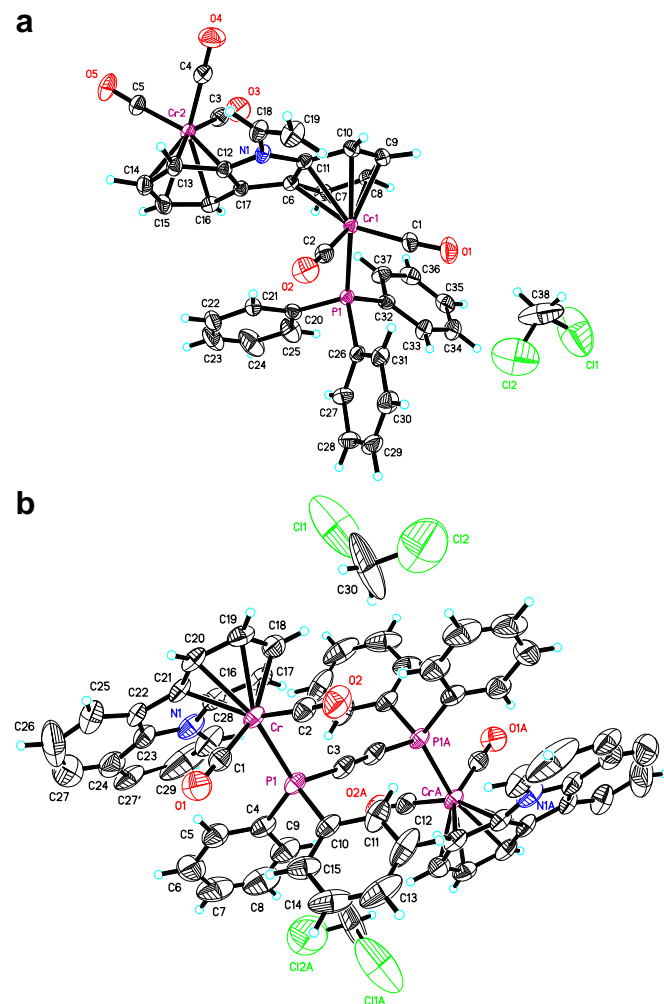


Fig. 1. ORTEP plot (50% thermal ellipsoids) of the X-ray crystal structures of compound **4**-dichloromethane (a) and **5**-dichloromethane (b). Selected bond lengths (\AA) and angles ($^\circ$) are: (a) Cr(1)–C(6): 2.269(4), Cr(1)–C(7): 2.225(4), Cr(1)–C(8): 2.220(4), Cr(1)–C(9): 2.179(4), Cr(1)–C(10): 2.216(4), Cr(1)–C(11): 2.245(4), Cr(2)–C(12): 2.292(4), Cr(2)–C(13): 2.238(4), Cr(2)–C(14): 2.190(5), Cr(2)–C(15): 2.205(5), Cr(2)–C(16): 2.219(4), Cr(2)–C(17): 2.272(4), Cr(1)–P(1): 2.3027(12), C(18)–C(19): 1.309(6), C(9)–Cr(1)–C(10): 37.62(16), C(9)–Cr(1)–C(8): 37.28(18), C(10)–Cr(1)–C(8): 67.95(16), C(9)–Cr(1)–C(7): 66.79(18), C(10)–Cr(1)–C(7): 80.41(16), C(8)–Cr(1)–C(7): 36.61(16), C(14)–Cr(2)–C(15): 37.56(18), C(14)–Cr(2)–C(13): 37.00(17), C(15)–Cr(2)–C(13): 67.17(18), C(14)–Cr(2)–C(16): 67.07(18), C(15)–Cr(2)–C(16): 36.56(17), C(16)–Cr(2)–C(13): 79.58(16). (b) Cr–P(1): 2.2694(14), C(28)–C(29): 1.260(13), P(1)–C(3): 1.781(5), C(3)–C(3)#1: 1.194(9); C(3)#1–C(3)–P(1): 175.8(6).

steric repulsion due to the bulky PPh_3 group. The N -vinyl group inclined toward Cr(1) by 32.4° relative to the carbazole plane and the double bond length of $1.309(6) \text{ \AA}$ is exceptionally longer than that observed for the others in this series.⁹ Complex **5** crystallizes together with two molecule of dichloromethane per complex and has an inversion center. This molecular structure is centrosymmetric with the 2 equiv organochromium units, which clearly adopts a pseudooctahedral geometry, as usually observed for many piano-stool complexes. The N -vinyl group bonded to the carbazole ring may exist in two or more positions, presumably due to some degree of disorder present in the structure at room temperature, it is still observed that the coordination sites at each of the chromium atoms are occupied by η^6 -phenyl ring, two CO ligands and phosphorus atom, respectively. $\text{P}=\text{C}=\text{P}$ chain is linear and behaves like the conjugated bridging ligand bounded to two metals, with a $\text{P}=\text{C}$ distance of $1.781(5) \text{ \AA}$ and a $\text{C}=\text{C}$ distance of $1.194(9) \text{ \AA}$. The Cr–P distance of $2.2694(14) \text{ \AA}$ is ca. 0.033 \AA shorter than that in **4**, indicating that the metal–metal

interaction across P–C≡C–P bridge strengthens the Cr–P bonds. Repeated attempts to grow X-ray-quality crystals of **6** failed, but its structural feature was made to allow comparisons with those of **5**. Despite distinguishing (CPh₂)₂ from (CHPh₂)₂, the same coordination sphere of the Cr atoms was completed by the η⁶-like π-carbazole ring and CO ligands in these two complexes.

2.2. Absorption properties

Fig. 2 shows the electronic absorption spectra of the complexes **4–6**. Each complex exhibits ligand-field (LF) in the 330–380 nm region¹² and metal-to-ligand charge transfer (MLCT) transitions in the 380–580 nm region.^{3b} These bands appear sensitive to the identity of the bridging ligand system: The LF band-width at half-height for **5** is much more than that for **6**, suggesting that ligand-to-metal (LM) transitions of large oscillator strength is present in **5** and is partially overlapped with the LF band.¹³

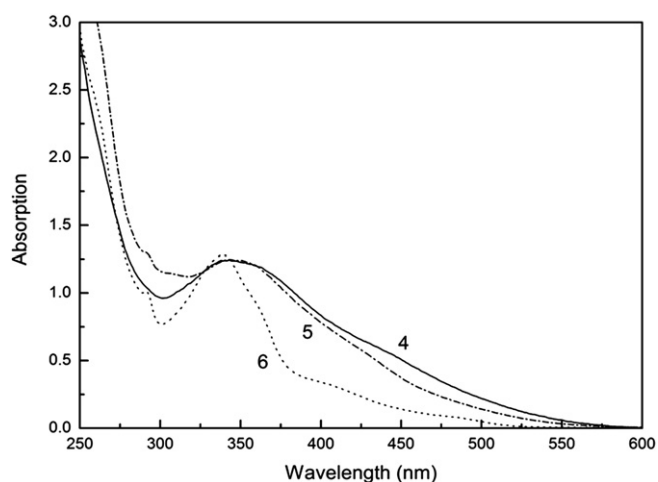


Fig. 2. UV-vis spectra of **4** (solid line), **5** (dashed-dot line), and **6** (dot line) measured in CH₂Cl₂ at a concentration of 10^{−4} M.

Similarly, the increase in the MLCT oscillator strength is also detected as the bridging ligand changed from (CHPh₂)₂ to (CPh₂)₂. As pointed out by Kanis et al.,¹³ the greater the electron density in the bridging region, the larger the oscillator strength in its absorption, as can be seen from **5** and **6**. Complex **5** possesses a more π-conjugated bridge, in which electron density is promoted from an orbital of primarily chromium (d-orbital) character to the π-antibonding orbital of (CPh₂)₂, and the cooperative effects of the LM and MLCT transitions are working well and thus allow the sufficient electronic communication between metal centers.

Meanwhile, a very strong electronic communication is found in complex **4**, specifically a rare example of homobimetallic complexes, where asymmetry occurred due to the presence of different ligands bound to the metals. The absorption spectrum of **4** shows a wide range of LF band and anomalously large MLCT oscillator strength compared with those observed from the corresponding symmetric complex **2**, as noted previously.^{9b} This result is assembly attributed to the organometallic push-pull architecture of **4**, in which the Cr(CO)₂PPh₃ and Cr(CO)₃ behave as the donor and acceptor, respectively.

2.3. Computational investigation

To gain insight into the charge-transfer component and the electronic asymmetry in **4**, one of the few structural examples with

the conjugated bridge bonded to two same but no equivalent metals, we have performed density functional theoretical (DFT) calculations based on the B3LYP/Lan12DZ level. The HOMO (−0.18978 a.u.) mainly centered on the two metal centers, whereas the LUMO (−0.07737 a.u.) is apparently populated on the carbazole. The population redistribution associated with the donation of electron density from the lone pair on the phosphorus atom to an empty hybrid orbital on the chromium is pronounced. Perhaps the more important observation from Fig. 3 is that a significant mixing among LMCT, MLCT, and ILCT is involved in the charge-transfer transition. On the basis of the TDDFT calculation, the lowest singlet is probably dominated by the MLCT transitions associated with a mixed contribution from the major HOMO and HOMO-1 (MOs 164–163) to the LUMO (MO 165). The changes in electronic populations between ground and singlet excited state are 0.035 electrons for Cr(CO)₂PPh₃, and 0.067 electrons for Cr(CO)₃, respectively. These electron density differences imply push-pull interaction between the two metal centers via the carbazole bridge. The corresponding calculations of **5** and **6** were not provided in our laboratory due to the limitation of the crystal structures, but it is also clear the electronic characteristics of the metal center in analogy with the situation in **4** and the conjugated bridging ligand acts as an intermediary between the 2 equiv chromium atoms to mediate the transfer of one electron through itself.

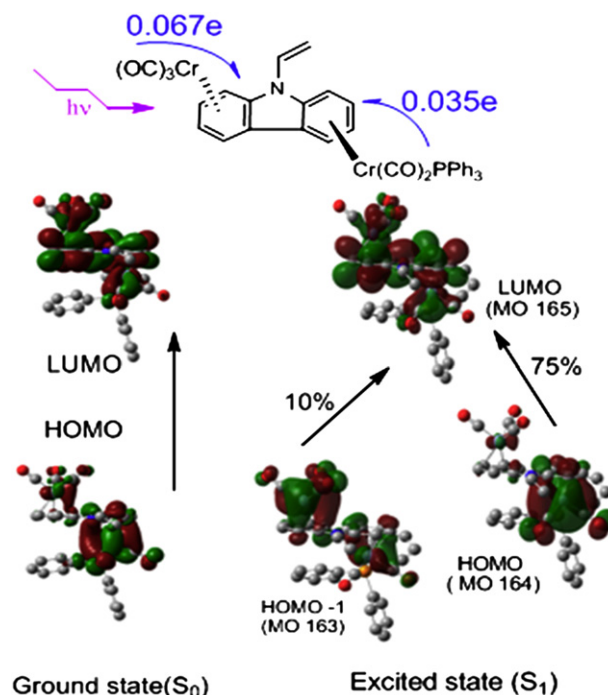


Fig. 3. Frontier molecular orbitals of **4** in the ground state (left), the first singlet excited state (right), the difference in electronic populations between ground state and excited state (top), calculated with TDDFT/DFT at the B3LYP/Lan12DZ level.

3. Conclusions

In conclusion, three dichromium complexes with (CPh₂)₂, (CHPh₂)₂, and carbazole bridges were designed and synthesized. The (CPh₂)₂ bridge is far more favorable for intramolecular electronic communication than the (CHPh₂)₂ bridge. An alternatively effective method for tuning the ligand-mediated metal–metal interaction is to introduce an appropriate ligand on the metal part. Detailed research on synthetic modification and the polymers containing this type of dichromium species as components for tunable molecular wires¹⁴ is under way.

4. Experimental

4.1. General considerations

All manipulations were carried out under a dry atmosphere of nitrogen with thoroughly dried and freshly distilled solvents. Cr(CO)₆ (99%) was purchased from Strem Chemicals and sublimed prior to use. Chromium *N*-vinylcarbazole complexes **1–3** were prepared in accordance with our previously published procedures. Elemental analyses were carried out on an Elementar Vario EL III analyzer (C, H, N) and TJARIS 1000 (Cr), respectively. Electron-impact mass spectra were recorded on a Micromass GCT (EI, 70 eV) mass spectrometer. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were acquired on a Bruker AVANCE 500 MHz spectrometer at 298 K, using C₆D₆ as the solvent and Me₄Si as an internal standard. IR spectra were performed on a Nicolet Magna-IR 550 instrument in KBr pellets. UV–vis spectra were obtained on a Varian Cary 500 spectrophotometer rebuilt by OLIS to incorporate computer control. Melting points were measured by a Reichert Thermopan melting point microscope without correction.

4.1.1. Synthesis of (CO)₃Cr(N-vinylcarbazole)Cr(CO)₂PPh₃ (4**).** (a) All photochemical synthesis were carried out with 200-W medium-pressure Hg lamp with the interference filters (10 nm band-pass) to isolate the irradiation wavelengths at 313, 365, and 405 nm. A mixture of 502 mg (1.08 mmol) of the dimetallic tricarbonyl complex **2** and 565 mg (2.15 mmol) of PPh₃ in 120 mL benzene was irradiated for 1.5 h, which was followed by the filtration through filter pulp and evaporation of the obtained dark violet solution. The crude oil was dissolved in ca. 5 mL of CH₂Cl₂, and the mixture was treated with hexanes to give a solid. The obtained mixture was then eluted with hexanes and redissolved in a 3:1 (v/v) CH₂Cl₂/*n*-hexane mixture (25 mL). The volume of the resulting solution was reduced to 20 mL after filtration. A small quantity of dark violet crystals **4** was obtained from this concentrated solution at –30 °C and the further purification was achieved by recrystallization. (b) Thermal conversions were conducted under an inert atmosphere with thoroughly dried and freshly distilled solvents and sealed in thin-walled glass tubes with avoiding sunlight. The mixture of monometallic tricarbonyl complex **1** (494 mg, 1.50 mmol) and monometallic PPh₃ complex **3** (845 mg, 1.50 mmol) was dissolved in dioxane (15 mL). The crude solution was freeze-thaw degassed and sealed in 2.5 cm (external diameter) tubes, which were subsequently placed in a thermostat at 65 °C for 12 h. After the removal from the bath, the corresponding mixture was precipitated in hexanes and filtered on a frit. Crystallization from CH₂Cl₂/*n*-hexane yields **4** (212 mg, 18% yield) as dark violet crystal at mp 184–186 °C (dec). ¹H NMR (500 MHz, C₆D₆), δ (ppm): 4.02 (t, 1H, *J*=6.02 Hz, CH₂–H), 4.08 (t, 1H, *J*=6.22 Hz, CH₂–H), 4.35 (dd, 1H, *J*=6.04, 3.43 Hz, Carb–H), 4.57 (d, 1H, *J*=7.78 Hz, Carb–H), 4.59 (t, 1H, *J*=6.32 Hz, Carb–H), 4.76 (d, 1H, *J*=15.38 Hz, Carb–H), 4.99 (d, 1H, *J*=6.77 Hz, Carb–H), 5.08 (d, 1H, *J*=15.65 Hz, Carb–H), 5.22 (dd, 1H, *J*=2.41, 3.60 Hz, Carb–H), 5.32 (d, 1H, *J*=16.41 Hz, Carb–H), 6.12 (dd, 1H, *J*=8.76, 6.92 Hz, CH–H), 7.46–7.43 (m, 6H, PPh₃–H), 6.98–6.94 (m, 9H, PPh₃–H). ¹³C NMR (125 MHz, C₆D₆), δ (ppm): 72.70(CH₂–C); 75.81 (CH–C); 83.94, 85.12, 86.16, 87.52, 87.96, 90.74, 93.23, 95.79, 108.99, 120.99, 123.10, 133.84 (Carb–C); 140.04, 140.31 (PPh₃–C); 234.44, 240.87 (CO–C). MS (EI, 70 eV; *m/z* (%)): 643 (M⁺–2CO, 1.06), 563 (M⁺–Cr(CO)₃, 1.80), 507 (M⁺–Cr(CO)₃–2CO, 20.16), 314 ((CrPPh₃)⁺, 100.00), 52 (Cr⁺, 81.67). IR (KBr): ν(CO), 1952, 1867, 1825 cm^{–1}. Anal. Calcd for C₃₇H₂₆Cr₂N₅P·CH₂Cl₂: C, 58.13; H, 3.57; N, 1.78; Cr, 13.26. Found: C, 58.01; H, 3.58; N, 1.83; Cr, 13.10.

4.1.2. Synthesis of (N-vinylcarbazole)Cr(CO)₂PC≡CPCr(CO)₂(N-vinylcarbazole) (5**).** Analogous to the operation used in the

preparation of **4** (see above), irradiation of Ph₂PCH≡CHPPh₂ (1890 mg, 4.80 mmol) and **1** (526 mg, 1.60 mmol) for 70 min gave a deep violet oil after filtration and evaporation. After redissolved in CH₂Cl₂ (5 mL) and precipitated with hexanes, a solid was afforded. Recrystallization from CH₂Cl₂/*n*-hexane yielded deep violet crystalline solid **5** (143 mg, 12%) at mp 126 °C (dec). ¹H NMR (500 MHz, C₆D₆), δ (ppm): 4.53 (dd, 2H, *J*=6.46, 6.62 Hz, CH₂–H), 4.68 (dd, 2H, *J*=6.36, 2.04 Hz, CH₂–H), 5.06 (m, 2H, Carb–H), 5.18 (m, 2H, Carb–H), 5.87 (s, 2H, CH–H), 6.50 (tt, 2H, *J*=9.40, 2.90 Hz, Carb–H), 6.89–6.93 (m, 4H, Carb–H), 7.00 (br s, 8H, PPh₂–H), 7.08 (t, 2H, *J*=7.71 Hz, Carb–H), 7.21 (br s, 8H, PPh₂–H), 7.26 (t, 2H, *J*=7.43 Hz, Carb–H), 7.32 (br s, 4H, PPh₂–H), 7.76 (dd, 2H, *J*=9.87, 9.48 Hz, Carb–H); ¹³C NMR (125 MHz, C₆D₆), δ (ppm): 73.75 (CH₂–C); 75.97 (CH–C); 85.02, 86.82, 90.71, 91.34, 93.13, 105.04, 107.33, 111.43, 119.93, 120.81, 122.18, 125.50, 127.22, 132.55, 132.77, 138.82, 141.92 (Carb–C); 110.18, 110.51 (C≡C); 234.43, 240.56 (CO–C). MS (EI, 70 eV; *m/z* (%)): 996 (M⁺, 73.06), 446 ((Ph₂PCH≡CHPPh₂+Cr)⁺, 39.80), 394 ((Ph₂PCH≡CHPPh₂)⁺, 21.02), 193 (N-vinylCarb⁺, 9.35), 52 (Cr⁺, 7.42). IR (KBr): ν(CO), 1950, 1870, 1820 cm^{–1}. Anal. Calcd for C₅₈H₄₂Cr₂N₂O₄P₂·2CH₂Cl₂: C, 61.76; H, 3.97; N, 2.40; Cr, 8.91. Found: C, 61.65; H, 3.93; N, 2.54; Cr, 8.80.

4.1.3. Synthesis of (N-vinylcarbazole)Cr(CO)₂PCH=CHPCr(CO)₂ (N-vinylcarbazole) (6**).** Irradiation of **1** (336 mg, 1.0 mmol) and Ph₂PCH=CHPPh₂ (1210 mg, 3.1 mmol) for 50 min gave a deep violet solid after precipitation of the deep violet oil from hexanes. Recrystallization from CH₂Cl₂/*n*-hexane afforded 148 mg (16%) of **6** as deep violet solid: mp 138 °C (dec). ¹H NMR (δ in C₆D₆) 4.27 (t, 2H, *J*=6.02 Hz, CH₂–H), 4.75 (t, 4H, *J*=9.26 Hz, Carb–H), 5.04 (dd, 2H, *J*=9.99, 15.72 Hz, CH₂–H), 5.18 (d, 2H, *J*=6.89 Hz, Carb–H), 5.77 (d, 2H, *J*=6.25 Hz, Carb–H), 6.33 (dd, 2H, *J*=9.09, 6.44 Hz, CH–H), 6.98 (d, 2H, *J*=8.1 Hz, Carb–H), 7.00 (br s, 12H, PPh₂–H), 7.04–7.08 (m, 4H, Carb–H), 7.40 (br s, 8H, PPh₂–H), 7.458 (d, 2H, *J*=7.59 Hz, Carb–H), 7.48 (t, 2H, *J*=7.37 Hz, Carb–H); ¹³C NMR (125 MHz, C₆D₆), δ (ppm): 71.96 (CH₂–C); 76.11 (CH–C); 86.36, 88.30, 93.21, 107.35, 111.45, 120.62, 121.62, 122.91, 124.45, 127.14, 128.69, 129.62, 133.53, 134.20, 138.84, 142.24 (Carb–C); 144.30 (CH=CH); 234.54, 240.75 (CO–C). MS (EI, 70 eV; *m/z* (%)): 998 (M⁺, 62.29), 448 ((Ph₂PCH=CHPPh₂+Cr)⁺, 51.35), 396 ((Ph₂PCH=CHPPh₂)⁺, 36.17), 193 (N-vinylCarb⁺, 9.33), 52 (Cr⁺, 9.41). IR (KBr): ν(CO), 1952, 1853 cm^{–1}. Anal. Calcd for C₅₈H₄₄Cr₂N₂O₄P₂: C, 69.74; H, 4.44; N, 2.80; Cr, 10.41. Found: C, 69.82; H, 4.40; N, 2.73; Cr, 10.36.

4.2. X-ray crystallographic structure determination of **4** and **5**

X-ray quality crystals of **4** were obtained from a saturated CH₂Cl₂/*n*-hexane solution upon cooling from 25 to –20 °C. Violet monocrystals of **5** were obtained by slow evaporation of a mixed CH₂Cl₂/*n*-hexane solution at –20 °C under argon. Compound **4** cocrystallized with one molecule of dichloromethane in the unit cell, while compound **5** cocrystallized with two molecules of dichloromethane. Relevant crystallographic information is summarized in Table 1. X-ray data were collected at 293 K on a Bruker Smart Apex CCD diffractometer with Mo K α graphite-monochromated radiation, $\lambda=0.71073$ Å, employing ω – 2θ technique. The structure was solved by direct methods using SHELXS97 and refined on the full-matrix least-squares method on all F² data using the program SHELXL97.¹⁵ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and refined using a riding model. CCDC-621208 and CCDC-621209 contain the supplementary crystallographic data for **4** and **5**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 0 1223 336033; e-mail: deposit@ccdc.cam.ac.uk].

Table 1
Details of data collection and structure refinement for **4** and **5**

| Compound | 4 | 5 |
|--|---|--|
| Chemical formula | C ₃₈ H ₂₈ Cl ₂ Cr ₂ NO ₅ P | C ₆₀ H ₄₆ Cl ₄ Cr ₂ N ₂ O ₄ P ₂ |
| Formula Mass | 784.48 | 1166.73 |
| Crystal system | Triclinic | Triclinic |
| <i>a</i> /Å | 11.0624(9) | 10.2235(16) |
| <i>b</i> /Å | 12.3186(10) | 11.3042(17) |
| <i>c</i> /Å | 14.4210(12) | 12.5891(19) |
| α /° | 65.7160(10) | 88.225(3) |
| β /° | 76.363(2) | 70.101(3) |
| γ /° | 77.2850(10) | 87.925(3) |
| Unit cell volume/Å ³ | 1723.9(2) | 1366.9(4) |
| Temperature/K | 293(2) | 293(2) |
| Space group | <i>P</i> 1 | <i>P</i> 1 |
| <i>Z</i> | 2 | 1 |
| Absorption coefficient, μ /mm ⁻¹ | 0.877 | 0.701 |
| No. of reflections measured | 10,227 | 7550 |
| No. of independent reflections | 7331 | 5287 |
| <i>R</i> _{int} | 0.0410 | 0.0649 |
| Final <i>R</i> ₁ values (<i>I</i> > 2 σ (<i>I</i>)) | 0.0691 | 0.0702 |
| Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2 σ (<i>I</i>)) | 0.2122 | 0.1716 |
| Final <i>R</i> ₁ values (all data) | 0.0827 | 0.1227 |
| Final <i>wR</i> (<i>F</i> ²) values (all data) | 0.2293 | 0.1925 |
| Goodness of fit on <i>F</i> ² | 1.084 | 0.886 |

4.3. Computational details

The electronic ground state and geometry optimization were computed by means of DFT-B3LYP method with LanL2DZ basis set using the Gaussian03.^{16a} In B3LYP, the functional used consists of the Becke three-parameter hybrid functional (B3) for the exchange part and the Lee, Yang and Parr (LYP)^{16b} for the correlation part. The LanL2DZ basis set was used for all the atoms (Cr, C, H, O, N, P). Since we treated transition metal, the used basis set seems large enough for reasonable describing the outer region of the metal and making the total molecular basis set still well balanced. The lowest excited state was calculated by TDDFT with the same basis set.

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Supplementary data

Supplementary data associated with this article include ¹H NMR and IR spectra of **4–6** and computational details of **4** described in this article. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.09.058.

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