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Thermally Stable Chromium(III) η^3-Allyl Complexes. Direct Structural Comparison of Neutral Chromium(II) and Cationic Chromium(III) η^3-Allyl Redox Isomers

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The first thermally stable chromium(III) η^3-allyl complexes have been prepared. Oxidation of neutral cyclopentadienylchromium(II) dicarbonyl η^3-allyl, η^3-crotyl, and η^3-cyclohexenyl complexes **1**−**3**, respectively, with $NOPF_6$, provides the corresponding cationic chromium(III) analogues **4**−**6**. The structure of the cationic complex **4** was confirmed in the solid state by X-ray crystallography and compared to the crystal structure of neutral Cr(II) complex **1**, which bears an identical ligand set. The cationic chromium(III) allyl complexes are thermally stable, but disproportionate at high concentration in donor solvents or in the presence of donor ligands: substitution of the carbonyl ligands with concomitant retention of the η^3-allyl moiety is unsuccessful under a range of reaction conditions. The reaction between cationic allyl complex **4** and the N-heterocyclic carbene, 1,3-bis(2,4,6,-trimethylphenyl)-imidazole-2-ylidene (IMes), leads to the formation of $IMesHPF_6$ and intractable chromium-containing products, while the reaction between the neutral complex **1** and IMes results exclusively in nucleophilic alkylation of the allyl ligand. Treatment of complex **4** with tertiary phosphines provides low yields of diamagnetic bis(phosphine)chromium(II) complexes.

Introduction

Organochromium chemistry has received considerable attention over the past two decades.[1] Notable among many interesting developments in the area of allylchromium chemistry, chromium(III) η^3-allyl complexes have been used as precursors in the preparation of olefin polymerization catalysts[2] and are putative intermediates in the stereoselective synthesis of homoallylic alcohols (i.e., the Nozaki−Hiyama−Kishi reaction).[1b−e,3] Despite such attractive applications, thermally stable chromium(III) complexes of this type are unreported.[4,5] Here, however, we report the preparation, isolation, and characterization of several *thermally stable cationic chromium(III)* η^3-allyl *complexes* and provide a direct structural comparison of the unsubstituted cationic complex with the corresponding neutral chromium(II) η^3-allyl analogue.

Results and Discussion

We recently reported a series of thermally stable chromium(II) η^3-allyl dicarbonyl complexes bearing a range of cyclopentadienyl and allyl ligands.[6] Reactivity studies reveal the compounds to be stable in toluene at reflux, unreactive toward trimethylamine *N*-oxide, and "terminally sensitive" to photolytic conditions. Treatment of chromium(II) allyl complex **1** with ferricinium, silver, or nitrosonium salts, however, provides crude reaction mixtures that show spectroscopic evidence for oxidation of the metal from chromium(II) to chromium(III). As monitored by solution infrared spectroscopy, the carbonyl absorptions for the neutral complex **1** in THF (1939 and 1869 cm^{-1}) shift to markedly higher frequency in the oxidized product (2070 and 2032 cm^{-1}), clearly indicative of stronger C−O bonds and weaker chromium-CO d→π^* back-bonding interactions. Unfortunately, the oxidized product does not persist in THF, acetonitrile, or acetone solutions: the higher energy carbonyl vibrations disappear completely after 3 h. To

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[1] (a) Jolly, P. W. *Acc. Chem. Res.* **1996**, *29*, 544−551. (b) Wessjohann, L. A.; Schied, G. *Synthesis* **1999**, 1−36. (c) Fürstner, A. *Chem. Rev.* **1999**, *99*, 991−1045. (d) Avalos, M. Babiano, R.; Cintas, P.; Jimenez, J. L. Palacios, J. C. *Chem. Soc. Rev.* **1999**, *28*, 169−177. (e) Takai, K.; Nozaki, H. *Proc. Jpn. Acad.*, *Ser. B* **2000**, *76B*, 123−131.

[2] Bade, O. M.; Blom, R.; Ystenes, M. *Organometallics* **1998**, *17*, 2524−2533.

[3] Selected recent references: (a) Inoue, M.; Suzuki, T.; Nakada, M. *J. Am. Chem. Soc.* **2003**, *125*, 1140−1141. (b) Fürstner, A.; Shi, N. *J. Am. Chem. Soc.* **1996**, *118*, 12349−12357. (c) Nowotny, S.; Tucker, C.; Jubert, C.; Knochel, P. *J. Org. Chem.* **1995**, *60*, 2762−2772. See also, references therein.

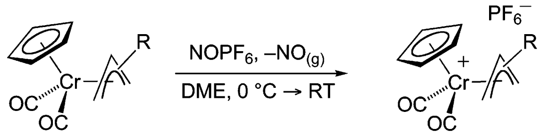
[4] All previously reported chromium(III) η^3-allyl complexes are unstable at room temperature. (a) $Cr(C_3H_5)_3$: Wilke, G.; Bogdanovic, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kröner, M.; Oberkirch, W.; Tanaka, K.; Steinrücke, E.; Walter, D.; Zimmermann, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 151−166. O'Brien, S.; Fishwick, M.; McDermott, B.; Wallbridge, M. G. H.; Wright, G. A. *Inorg. Synth.* **1972**, *13*, 73−79. (b) $CpCr(C_3H_5)_2$: Nieman, J.; Pattiasina, J. W.; Teuben, J. H. *J. Organomet. Chem.* **1984**, *262*, 157−169. Angermund, K.; Döhring, A.; Jolly, P. W.; Krüger, C.; Romão, C. C. *Organometallics* **1986**, *5*, 1268−1269. (c) $Cp'Cr(C_3H_5)_2$, $Cr(C_3H_5)_2Cl$: Betz, P.; Döhring, A.; Emrich, R.; Goddard, R.; Jolly, P. W.; Krüger, C.; Romão, C.; Schönfelder, K. U.; Tsay, Y.-H. *Polyhedron* **1993**, *12*, 2651−2662.

[5] Tentatively assigned chromium(III) η^3-allyl complexes have also been proposed as reactive intermediates. (a) (Cp-*ansa*-amino)Cr-$(C_3H_5)_2$: Döhring, A.; Göhre, J.; Jolly, P. W.; Kryger, B.; Rust, J.; Verhovnik, G. P. J. *Organometallics* **2000**, *19*, 388−402. (b) CpCr-(benzamidinato)-(C_3H_5): Gallant, A. J.; Smith, K. M.; Patrick, B. O. *Chem. Commun.* **2002**, 2914−2915.

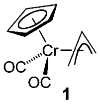
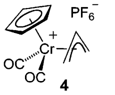
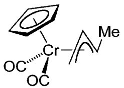
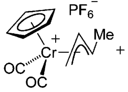
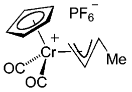
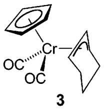
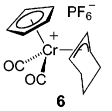
[6] Norman, D. W.; Ferguson, M. J.; Stryker, J. M. *Organometallics* **2004**, *23*, 2015−2019.

10.1021/om050415z CCC: $30.25

Table 1. Synthesis of Cationic η^3-Allyl Complexes 4–6 (eq 1)[a]



(1)

Entry	Substrate	Product(s)	ν_{CO}[b]	Yield[c]
1	 **1**	 **4**	2070 2032	82
2	 **2**	 +  **5**–*exo* **5**–*endo*	2065 2040 2031 2022	70
3	 **3**	 **6**	2039 2002	96

[a] Reaction conditions: NOPF$_6$, DME, 0 °C RT, 20 min. [b] Infrared spectra recorded as a Nujol mull, cm^{-1}. [c] Isolated yield (%) of analytically pure material.

stabilize the nitrosonium oxidant[7] and to avoid prolonged exposure to donor solvent, the oxidation reaction was conducted in 1,2-dimethoxyethane (DME), a solvent in which the chromium(III) product is only sparingly soluble. Thus, treatment of the chromium(II) η^3-allyl complex **1** with nitrosonium hexafluorophosphate in DME at 0 °C leads to considerable effervescence and precipitation of an analytically pure paramagnetic green solid, subsequently identified as cationic chromium(III) η^3-allyl complex **4** (eq 1 and Table 1, entry 1). Infrared spectroscopy of this solid as a Nujol mull shows carbonyl stretching frequencies at 2070 and 2032 cm^{-1}, with no evidence of the neutral η^3-allyl dicarbonyl complex. It is interesting to note that addition of NOPF$_6$ to complex **1** does not lead to a nitrosyl complex, as reported for the corresponding molybdenum analogue.[7b] The smaller ionic radius of chromium apparently permits one-electron oxidation by nitrosonium ion, but not the subsequent coordination of the co-generated nitric oxide.[8]

This methodology is readily extended to the oxidation of substituted chromium(II) η^3-allyl complexes. Thus, treatment of η^3-crotyl and η^3-cyclohexenyl complexes **2** and **3** with NOPF$_6$ in DME leads to the oxidized congeners **5** and **6**, respectively (Table 1, entries 2 and 3). Oxidation of the more soluble indenyl η^3-allyl complex,[6] however, does not provide a precipitate, and no tractable reaction product can be isolated from solution. The infrared spectra of complexes **4** and **6** each show two carbonyl stretching frequencies, suggesting the presence of a single stereoisomer, whereas the spectrum of complex **5** displays four high-energy absorptions, implying the presence of both *endo* and *exo* isomers.[9] Both chromium(III) η^3-allyl complexes **4** and **5** are green to yellow-green in color; the η^3-cyclohexenyl complex **6**, however, is an orange-red powder. This contrast in color suggests the possibility of unique bonding interactions for the cyclohexenyl ligand, including the possibility of an agostic interaction between one methylene C–H bond of the η^3-cyclohexenyl ligand and the now unsaturated 17-electron metal center. Indeed, the X-ray crystal structure[6] of the *neutral* η^3-cyclohexenyl precursor **3** reveals the distance between the metal and one distal (nonallylic) methylene hydrogen to be just 3.22 Å; upon one-electron oxidation, this distance may contract sufficiently to create an agostic bonding interaction. Alternatively, the difference in color may simply result from the unique 1,3-bis(anti) substitution pattern imposed by the endocyclic disposition of the η^3-allyl moiety.

Single crystals of the unsubstituted cationic allyl complex **4** were deposited directly from the oxidation reaction conducted at higher dilution, and the structure was confirmed by X-ray crystallography (Figure 1).[10] While the solid state structure of this complex is in itself unremarkable, more notable is the opportunity to compare this cationic chromium(III) complex with the solid state structure of the neutral but otherwise identical chromium(II) complex **1** (Table 2).[6] The structures, while superficially similar, differ in a number of significant parameters. The chromium responds to the oxidation by marginally decreasing the metal–carbon bond distances for the two terminal allyl positions to 2.220(3) Å from 2.231(5) and 2.239(5) Å in complex **1**, but the distance between the allyl central carbon and the chromium center increases to 2.151(4) Å from 2.108(4) Å. These differences in bond distances alter the dihedral angle between the planes containing the allyl ligand and the cyclopentadienyl, respectively, which increases by more than 5° in the oxidized complex. The most striking difference between the two η^3-allyl complexes, however, is manifest in the dihedral angle between the plane containing the Cr(CO)$_2$ fragment and that of the cyclopentadienyl ring: in cationic complex **4**, the Cr(CO)$_2$ plane is tilted fully 10° closer to the plane of the ring than it is in neutral complex **1**. This substantial relaxation of the roughly square pyramidal coordination sphere may be attributed to the reduction in d→π* back-donation from the oxidized metal center to the ancillary carbonyl and allyl ligand. The location of the counterion in or just under the cleft formed between the allyl and carbonyl ligands (Figure 1), however, suggests that the ancillary ligands shift toward the cyclopentadienyl ring in order to accommodate a closer association of counteranion and the cationic chromium center. Unsurprisingly, with the

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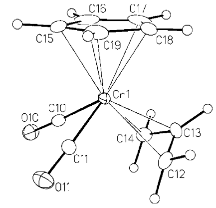
[7] Liebeskind[7a] has established that nitrosonium salts are unstable in most donor solvents, with the notable exception of DME at 0 °C. Indeed, nitrosonium salts in DME are persistent enough to react with cyclopentadienylmolybdenum η^3-allyl dicarbonyl compounds to provide the corresponding η^3-allyl nitrosylcarbonyl complexes in much higher yields than originally reported by Faller.[7b] (a) Cosford, N. D. P.; Liebeskind, L. S. *Organometallics* **1994**, *13*, 1498–1503. (b) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 3388–3389.

[8] Similar reactivity has been observed for other chromium(II) complexes upon nitrosonium ion oxidation to the chromium(III) analogues: (a) Shen, J. K.; Freeman, J. W.; Hallinan, N. C.; Rheingold, A. L.; Arif, A. M.; Ernst, R. D.; Basolo, F. *Organometallics* **1992**, *11*, 3215–3224. (b) Connelly, N. G.; Johnson, G. A. *J. Organomet. Chem.* **1974**, *77*, 341–344.

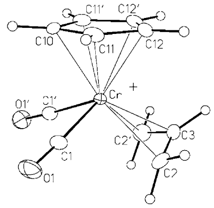
[9] Elemental analysis of complex **5** confirms the compositional homogeneity, supporting the tentative assignment of an *endo*/*exo* mixture of allyl stereoisomers.

[10] Crystal data for complex **4** ($C_{10}H_{10}CrF_6O_2P\cdot 0.5C_4H_{10}O_2$, −80 °C); orthorhombic, *Cmcm* (No. 63), $a = 10.4586(10)$ Å, $b = 11.5544(11)$ Å, $c = 26.008(3)$ Å, $V = 3142.9(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.709$ g cm^{-3}, $\mu = 0.902$ mm^{-1}, $R_1 = 0.0448$ ($F_o^2 \geq 2\sigma(F_o^2)$), $wR_2 = 0.1189$ (all data).

Table 2. Selected Bond Lengths (Å), Angles (deg), and Dihedral Angles between Planes (deg) for η^3-Allyl Complexes 1 (neutral) and 4 (cation)[a]



Neutral Cr(II) η^3-allyl complex **1**



Cationic Cr(III) η^3-allyl complex **4**[b]

Bond lengths (Å)[c]		**Bond lengths (Å)**	
Cr(1)-C(10)	1.814(6)	Cr-C(1)	1.901(3)
Cr(1)-C(11)	1.817(5)		
Cr(1)-C(12)	2.231(5)	Cr-C(2)	2.220(3)
Cr(1)-C(13)	2.108(4)	Cr-C(3)	2.151(4)
Cr(1)-C(14)	2.239(5)		
Cr(1)-C(15)	2.164(5)	Cr-C(10)	2.164(4)
Cr(1)-C(16)	2.178(6)	Cr-C(11)	2.184(3)
Cr(1)-C(17)	2.231(5)	Cr-C(12)	2.215(3)
Cr(1)-C(18)	2.215(5)		
Cr(1)-C(19)	2.190(5)		
O(10)-C(10)	1.168(6)	O(1)-C(1)	1.125(4)
O(11)-C(11)	1.155(6)		
Bond angles (deg)[c]		**Bond angles (deg)**	
C(11)-Cr-C(10)	83.4(2)	C(1)-Cr-C(1')	87.72(19)
C(11)-Cr-C(12)	72.6(2)	C(1)-Cr-C(2)	77.51(14)
C(11)-Cr-C(13)	107.9(2)	C(1)-Cr-C(3)	113.38(12)
C(11)-Cr-C(14)	113.4(2)	C(1)-Cr-C(2')	122.30(14)
C(11)-Cr-C(19)	89.0(2)	C(1)-Cr-C(11)	81.69(12)
C(12)-Cr-C(18)	93.7(2)	C(2)-Cr-C(12)	92.90(13)
C(13)-Cr-C(18)	88.8(2)	C(3)-Cr-C(12)	88.09(14)
C(12)-C(13)-C(14)	118.8(5)	C(2)-C(3)-C(2')	120.0(5)
Dihedral angle planes (deg)[c]		**Dihedral angle planes (deg)**	
$Cr(CO)_2$ / allyl	2.8(8)	$Cr(CO)_2$ / allyl	1.8(8)
$Cr(CO)_2$ / Cp	38.24(18)	$Cr(CO)_2$ / Cp	28.27(17)
allyl / Cp	35.5(6)	allyl / Cp	30.1(6)

[a] Complete listings of bond lengths and angles are provided as Supporting Information. [b] Counterion omitted for clarity. [c] Tabulation taken from one of two independent molecules; values for the more disordered molecule are available as Supporting Information.

reduction in d→π* back-donation, the chromium−CO bond distances in complex **4** increase to 1.901(3) Å, notably longer than in the lower valent complex **1** (1.814(6) and 1.817(5) Å). Accordingly, the C−O bond lengths of the cationic complex are approximately 3% shorter than those in complex **1**, resulting in an almost 150 cm^{-1} increase in the average carbonyl stretching frequency in the infrared spectrum of the cationic complex. Such changes in bond distances and infrared absorptions have been previously reported for redox pairs of chromium dicarbonyl complexes, albeit with entirely different ligand sets.[8b,11]

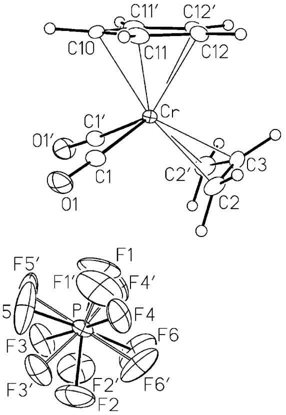
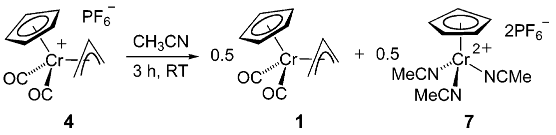


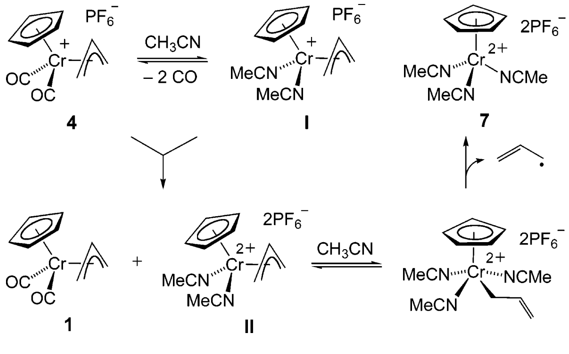
Figure 1. Solid state molecular structure of complex **4** showing the disordered PF_6 counterion; 0.5 equiv of interstitial DME is omitted. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. See Table 2 for selected bond lengths and angles of the cation. Complete listings of bond lengths and angles are available as Supporting Information.

Cationic η^3-allyl complexes **4**−**6** are indefinitely stable as solids at room temperature, unique among previously reported chromium(III) η^3-allyl compounds.[4,5] In donor solvents, however, the complexes are susceptible to rapid disproportionation. In acetonitrile, for example, complex **4** is completely consumed after 3 h to give a 1:1 mixture of the neutral η^3-allyl complex **1** and the novel dicationic cyclopentadienylchromium(III) tris(acetonitrile) complex **7** in high yield (eq 2). The presence of 1,5-hexadiene (unquantified) in the crude reaction mixture was confirmed by gas chromatography, presumably arising from homolytic cleavage of the allyl ligand. The mechanism of this reaction is presumed to involve equilibrium dissociation of the carbonyl ligands to give the cationic bis(acetonitrile) complex **I** (Scheme 1). This relatively electron rich intermediate can then reduce the remaining dicarbonyl cation **4**, ultimately producing a 1:1 mixture of the neutral η^3-allyl complex **1** and the thermally unstable dicationic chromium(IV) allyl intermediate **II**. Subsequent association of acetonitrile followed by homolysis of the consequent η^1-allyl ligand leads to the formation of 1,5-hexadiene and the observed dicationic tris(acetonitrile) complex **7**. Consistent with this mechanism, the rate of the disproportionation is reduced at higher dilution. The structural assignment is supported by independent synthesis: treatment of the known dichloro dimer $[(\eta^5-C_5H_5)CrCl_2]_2$[4c] with 4 equiv of silver hexafluorophosphate in acetonitrile affords the tris(acetonitrile) complex **7** in high yield.



(2)

Scheme 1



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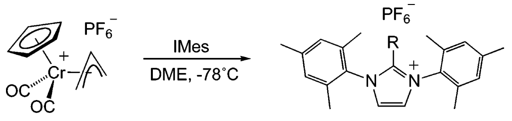
(11) Orpen, A. G.; Connelly, N. G. *Organometallics* **1990**, *9*, 1206−1210. Adams, C. J.; Bartlett, I. M.; Connelly, N. G.; Harding, D. J.; Hayward, O. D.; Martín, A. J.; Orpen, A. G.; Quayle, M. J.; Rieger, P. H. *J. Chem. Soc., Dalton Trans.* **2002**, 4281−4288.

Our attempts to induce substitution of the carbonyl ligands in cationic complex **4** without concomitant redox disproportionation have met no notable success. Upon treatment with trimethylamine *N*-oxide, a suspension of complex **4** in DME provides only an intractable product mixture, while heating a suspension in toluene gives a variable amount of the neutral η^3-allyl dicarbonyl complex **1** and an uncharacterizable blue material. Displacement of the carbonyl ligands with strong neutral donors also failed to yield products retaining the allyl ligand. For example, the reaction of complex **4** with the stable N-heterocyclic carbene 1,3-bis(2,4,6,-trimethylphenyl)imidazole-2-ylidene (IMes) gave unidentified metal-containing product(s). A diagmagnetic organic fraction was also isolated, which by ^{1}H NMR spectroscopy proved to be mostly the protonated carbene, IMesHPF$_6$ (**III**), a known compound,[12] along with a trace of the tentatively identified allylated analogue, 1,3-bis(2,4,6,-trimethylphenyl)-2-(1-propenyl)imidazolium hexafluorophosphate, compound **IV** (eq 3). The major reaction pathway thus appears to be the deprotonation of the starting complex (presumably at the allyl ligand), accompanied by a less favorable nucleophillic addition to the η^3-allyl terminal position. By way of comparison, the reaction between the *neutral* η^3-allyl complex **1** and IMes surprisingly gives the diamagnetic zwitterionic alkylation product **8** in excellent yield (eq 4). The structure of this complex was determined by spectroscopic analysis and confirmed in the solid state by X-ray crystallography (Figure 2).[13,14] Although the reactions with IMes do not lead to decarbonylation of either the neutral or cationic η^3-allyl complexes, the products reveal unprecedented ligand-centered reactivity for the stabilized carbene, which more typically functions as an ancillary ligand in organometallic systems.[15,16] It is not obvious why the more electrophilic chromium(III) complex **4** favors deprotonation over nucleophilic addition, despite the obviously low activation barrier for the nucleophilic pathway in the neutral congener.



(3)

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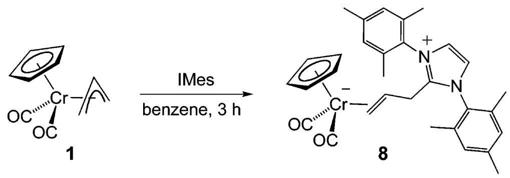
III (R = H); **IV** (R = C_3H_5)



(4)

1

8

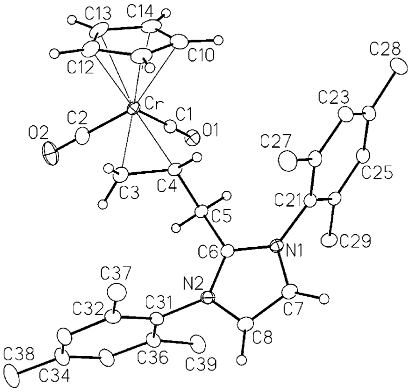
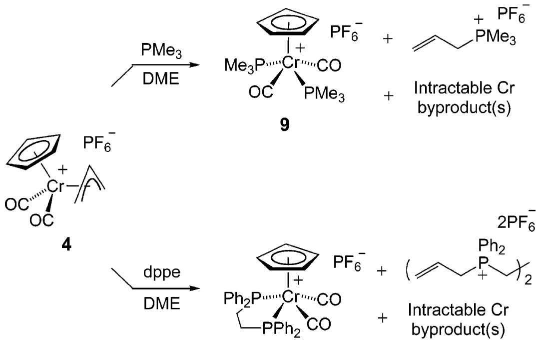


Figure 2. Solid state molecular structure of complex **8**; 0.5 equiv of interstitial THF is omitted. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Selected bond lengths (Å) and angles (deg): Cr−C(1) = 1.789(2), Cr−C(2) = 1.798(3), Cr−C(3) = 2.150(2), Cr−C(4) = 2.140(2), Cr−C(10) =2.231(3), Cr−C(11) = 2.228(2), Cr−C(12) = 2.223(2), Cr−C(13) = 2.217(2), Cr−C(14) = 2.218(3), O(1)−C(1) = 1.182(3), O(2)−C(2) = 1.180(3), C(3)−C(4) = 1.414(3), C(4)−C(5) = 1.523(3), C(5)−C(6) = 1.490(3), C(7)−C(8) = 1.340(3), N(1)−C(6) = 1.343(3), N(2)−C(6) = 1.341(3); C(1)−Cr−C(10) = 102.89(10), C(1)−Cr−C(2) = 85.89(10), C(1)−Cr−C(3) = 109.99(9), C(1)−Cr−C(4) = 84.07(9), C(3)−Cr−C(4) = 38.48(8), C(3)−C(4)−C(5) = 119.10(19), C(4)−C(5)−C(6) = 110.27(17), N(1)−C(6)−N(2) = 106.85(17).

Scheme 2



9

4

10

The investigation of phosphine substitution was equally disappointing. In contrast to the chemistry of the neutral chromium(II) η^3-allyl complex, the reaction of chromium(III) complex **4** with monodentate or bidentate tertiary phosphine proceeds at or below room temperature, but leads only to the isolation of diamagnetic cationic cyclopentadienylchromium(II) bis(phosphine) complexes in low yield (Scheme 2). Thus, treatment of a suspension of complex **4** in DME with 2 equiv of trimethylphosphine leads to the formation of a yellow-green solid, identified spectroscopically as the *trans*-bis(trimethylphosphine)cyclopentadienylchromium(II) dicarbonyl cation **9**. A second product, isolated from the supernatant, was determined to be the known allyltrimethylphosphonium hexafluorophosphate by spectroscopic comparison to authentic material prepared in-

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(12) The major product, IMesHPF$_6$, was identified by comparison with an authentic sample prepared independently: Arduengo, A. J., III; Gamper, S. F.; Tamm, M.; Calabrese, J. C.; Davidson, F.; Craig, H. A. *J. Am. Chem. Soc.* **1995**, *117*, 572−573. The trace product was tentatively identified based on broad ^{1}H NMR signals between 5.0 and 6.5 ppm, indicative of a terminal olefin.

(13) Crystal data for complex **8** ($C_{31}H_{34}CrN_2O_2\cdot0.5C_4H_8O$, −80 °C); monoclinic, *I*2/*a* (an alternate setting of *C*2/*c* [No. 15]), a = 42.1994(18) Å, b = 8.4552(4) Å, c = 37.1949(16) Å, β = 115.8337(7)°, V = 11945.0(9) Å^3, Z = 16, ρ_{calcd} = 1.234 g cm^{-3}, μ = 0.416 mm^{-1}, R_1 = 0.0482 ($F_o^2 \geq 2\sigma(F_o^2)$), wR_2 = 0.1396 (all data).

(14) Although anionic 18e$^-$ Cr(0) complexes of the form η^5-CpCrL$_2$(olefin)$^-$ appear to be unprecedented, corresponding *neutral* (η^6-arene)CrL$_2$(olefin) analogues have been reported; see: Angelici, R. J.; Busetto, L. *Inorg. Chem.* **1968**, *7*, 1935−1936, and references therein.

(15) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309. Herrmann, W. A. *Adv. Organomet. Chem.* **2002**, *48*, 1−69.

(16) The high nucleophilicity of the N-heterocyclic carbene toward the neutral allyl complex **1** is both noteworthy and surprising; no reaction is observed upon addition of excess PMe$_3$, even at 65 °C.

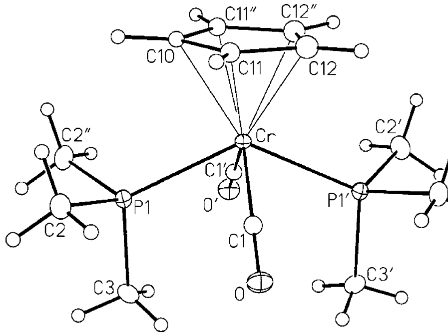
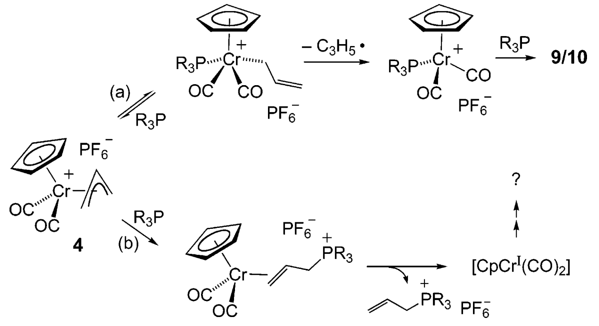


Figure 3. Solid state molecular structure of complex **9**, showing only the cationic fragment. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Selected bond lengths (Å) and angles (deg): Cr−C(1) = 1.843(3), Cr−P(1) = 2.3509(8), Cr−C(10) = 2.193(5), Cr−C(11) = 2.199(4), Cr−C(12) = 2.1997(5), O−C(1) = 1.150(4); C(1)−Cr−C(10) = 118.70(8), C(1)−Cr−C(1′) = 111.26(17), P(1)−Cr−P(1′) = 129.66(4), P(1)−Cr−C(1) = 76.11(4), P(1)−Cr−C(10) = 83.45(13).

Scheme 3



dependently.[17] Similar reaction conditions lead to the formation of *cis*-[1,2-bis(diphenylphosphino)ethane]-cyclopentadienylchromium(II) dicarbonyl cation **10** from treatment with 1 equiv of bis(diphenylphophino)ethane, along with the tentatively assigned doubly allylated phosphonium salt. Complexes **9** and **10** presumably arise from the association of one phosphine to the metal with concomitant isomerization of the allyl ligand from η^3- to η^1-hapticity (Scheme 3, path a). Subsequent homolytic loss of allyl radical and association of a second phosphine provide the observed product. The allylphosphonium salts must then result from *an independent pathway* triggered by nucleophilic addition of phosphine to the allyl ligand (Scheme 3, path b), followed by dissociation of the alkene from the now Cr(I) center. Unfortunately, no other tractable metal-containing products could be isolated from these reactions, leaving the fate of the reduced chromium species as yet undetermined. Although NMR spectroscopy was sufficient to assign the stereochemistry about the metal center, the structural determination of both complexes was complemented by X-ray crystallography (Figures 3, 4).[18,19] *cis*- and *trans*-Bis(phosphine) complexes similar to **9** and **10** have been previously reported.[8,20−22]

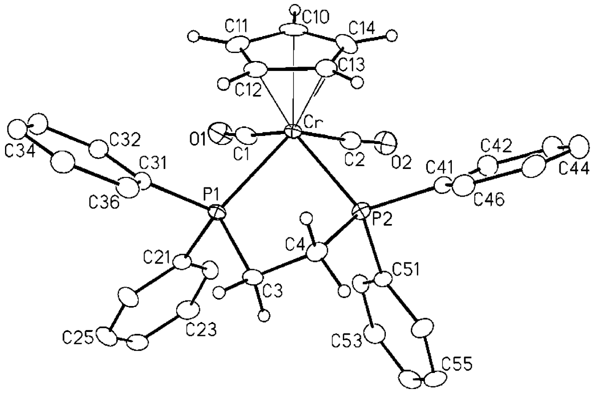


Figure 4. Solid state molecular structure of complex **10** showing only the cationic fragment; 1.5 equiv of interstitial acetone is omitted. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Selected bond lengths (Å) and angles (deg): Cr−C(1) = 1.854(6), Cr−C(2) = 1.834(5), Cr−P(1) = 2.3994(13), Cr−P(2) = 2.3889(13), Cr−C10, 2.171(5), Cr−C(11) = 2.186(5), Cr−C(12) = 2.234(5), Cr−C(13) = 2.242(5), Cr−C(14) = 2.187(5), O(1)−C(1) = 1.146(7), O(2)−C(2) = 1.162(7), P(1)−C(3) = 1.866(4), C(3)−C(4) = 1.511(7), P(2)−C(4) = 1.820(5); C(1)−Cr−C(10) = 88.1(2), C(1)−Cr−C(2) = 78.6(2), P(1)−Cr−C(12) = 87.29(14), P(2)−Cr−C(13) = 82.43(14), P(1)−Cr−P(2) = 77.84(5), P(1)−C(3)−C(4) = 110.9(3), P(2)−C(4)−C(3) = 105.7(3).

Conclusion

A general methodology for the preparation and isolation of cationic cyclopentadienylchromium(III) η^3-allyl dicarbonyl complexes has thus been developed. These new compounds are remarkably thermally stable, but have a strong tendency to disproportionate at sufficient concentration in donor solvents. The thermal stability is reasonably attributed to the presence of the strongly π-acidic carbonyl ligands, which maintain the allyl ligand in the thermodynamically most stable η^3-bonding mode. In more electron-rich chromium(III) η^3-allyl complexes,[4,5] the allyl ligand is likely equilibrating between η^3- and η^1-hapticity, allowing the less strongly bound η^1-isomer to undergo facile chromium−carbon bond homolysis and reduction to chromium(II). Comparison of the structures of the neutral and cationic η^3-allyl complexes reveals a significant change in the coordination geometry of the cation, with the carbonyl ligands positioned significantly closer to the cyclopentadienyl ring than observed in the neutral chromium(II) analogue. Despite the lability of the carbonyl ligands in chromium(III) complexes **4**−**6**, we have as yet been unable to modify the ligand set without concomitant loss of the allyl fragment.

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(17) Cardaci, G. *J. Chem. Soc., Dalton Trans.* **1984**, 815−818.

(18) Crystal data for complex **9** ($C_{13}H_{23}CrF_6O_2P_3$, −80 °C); orthorhombic, *Pmmn* (No. 59), a = 10.7360(7) Å, b = 11.0577(7) Å, c = 8.0243(5) Å, V = 952.61(10) Å^3, Z = 2, ρ_{calcd} = 1.639 g cm^{-3}, μ = 0.913 mm^{-1}, R_1 = 0.0333 ($F_o^2 \geq 2\sigma(F_o^2)$), wR_2 = 0.0869 (all data).

(19) Crystal data for complex **10** ($C_{33}H_{29}CrF_6O_2P_3 \cdot 1.5C_3H_6O$, −80 °C); orthorhombic, $P2_12_12_1$ (No. 19), a = 12.0893(10) Å, b = 16.7108(14) Å, c = 19.4470(16) Å, V = 3928.7(6) Å^3, Z = 4, ρ_{calcd} = 1.359 g cm^{-3}, μ = 0.477 mm^{-1}, R_1 = 0.0676 ($F_o^2 \geq 2\sigma(F_o^2)$), wR_2 = 0.1911 (all data).

(20) Schubert, U.; Ackermann, K.; Janta, R.; Voran, S.; Malisch, W. *Chem. Ber.* **1982**, *115*, 2003−2008.

(21) (a) Cooley, N. A.; MacConnachie, P. T. F.; Baird, M. C. *Polyhedron* **1988**, *7*, 1965−1972. (b) Watkins, W. C.; Hensel, K.; Fortier, S.; Macartney, D. H.; Baird, M. C. *Organometallics* **1992**, *11*, 2418−2424.

(22) Salsini, L.; Pasquali, M.; Zandomeneghi, M.; Festa, C.; Leoni, P.; Braga, D.; Sabatino, P. *J. Chem. Soc., Dalton Trans.* **1990**, 2007−2012.

Experimental Section

General Procedures. All manipulations of air-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-filled drybox. Ethereal and hydrocarbon solvents were purified by distillation from sodium or potassium benzophenone ketyl. Acetonitrile was purified by distillation from calcium hydride and degassed. Acetone was dried from boric anhydride and degassed. Infrared (IR) spectra were obtained in solution (KBr solution cells) or in the solid state (as Nujol mulls on KBr disks) and are reported in wavenumbers (cm^{-1}) calibrated to the 1601 cm^{-1} absorption of polystyrene. Chemical shifts are reported in the δ scale, referenced to residual protiated solvent. Combustion analyses were performed by the University of Alberta Microanalysis Laboratory. *Some of the chromium compounds failed to afford consistent elemental analysis, even when using highly purified crystalline samples suitable for X-ray crystallography*.

[(η^3-Allyl)(η^5-cyclopentadienyl)dicarbonylchromium]-PF_6·$(DME)_{0.5}$, 4. In a Schlenk flask under an inert atmosphere, (η^5-C_5H_5)$Cr(CO)_2(C_3H_5)$, **1**[6] (405 mg, 1.89 mmol), was dissolved in 20 mL of DME and cooled to 0 °C. A solution of $NOPF_6$ (331 mg, 1.89 mmol) in 15 mL of DME at 0 °C was added via cannula. Immediately a color change from orange to green was observed with effervescence and formation of a green precipitate. After stirring for 20 min, the suspension was warmed to room temperature and 20 mL of diethyl ether added. The precipitate was collected on a frit, washed with 2 × 10 mL of diethyl ether, and dried to give allylchromium complex **4** as a green DME solvate (625 mg, 82%). IR (ν_{CO}, cm^{-1}, Nujol): 2070, 2032. Anal. Calcd for $C_{10}H_{10}CrO_2PF_6$·0.5DME: C, 35.66; H, 3.74. Found: C, 34.87; H, 3.80. Crystals suitable for analysis by X-ray diffraction were grown from an equimolar solution of complex **1** and $NOPF_6$ in dilute DME (~46 mM), upon standing undisturbed at RT for 16 h.

[(η^3-Crotyl)(η^5-cyclopentadienyl)dicarbonylchromium]-PF_6, 5. In a Schlenk flask under an inert atmosphere, (η^5-C_5H_5)$Cr(CO)_2(C_4H_7)$, **2**[6] (46 mg, 0.202 mmol), was dissolved in 5 mL of DME and cooled to 0 °C. A solution of $NOPF_6$ (35 mg, 0.202 mmol) in 10 mL of DME at 0 °C was added via cannula. Immediately a color change from yellow to light green was observed with concomitant effervescence and formation of a light green precipitate. After stirring for 20 min, the suspension was warmed to room temperature and 10 mL of diethyl ether added. The precipitate was collected on a frit, washed with 2 × 5 mL of diethyl ether, and dried to give crotylchromium complex **5** as a pure yellow-green powder (53 mg, 70%). IR (ν_{CO}, cm^{-1}, Nujol): 2065, 2040, 2031, 2022. Anal. Calcd for $C_{11}H_{12}CrO_2PF_6$: C, 35.40; H, 3.24. Found: C, 35.34; H, 2.92.

[(η^3-Cyclohexenyl)(η^5-cyclopentadienyl)dicarbonylchromium]PF_6, 6. In a Schlenk flask under an inert atmosphere, (η^5-C_5H_5)$Cr(CO)_2(C_6H_9)$, **3**[6] (46 mg, 0.180 mmol), was dissolved in 5 mL of DME and cooled to 0 °C. A solution of $NOPF_6$ (35 mg, 0.197 mmol) in 10 mL of DME at 0 °C was added via cannula. Immediately a color change from yellow to orange was observed with concomitant effervescence and formation of an orange-red precipitate. After stirring for 20 min, the suspension was warmed to room temperature and 10 mL of diethyl ether added. The precipitate was collected on a frit, washed with 2 × 5 mL of diethyl ether, and dried to give cyclohexenylchromium complex **6** as an orange-red powder (69 mg, 96%). IR (ν_{CO}, cm^{-1}, Nujol): 2039, 2002. Anal. Calcd for $C_{13}H_{14}CrO_2PF_6$: C, 39.11; H, 3.53. Found: C, 38.60; H, 3.42.

[(η^5-Cyclopentadienyl)tris(acetonitrile)chromium]-$(PF_6)_2$, 7, from [(η^3-allyl)(η^5-cyclopentadienyl)dicarbonylchromium]PF_6·$(DME)_{0.5}$. Allylchromium(III) complex **4** (22 mg, 0.061 mmol) was dissolved in 5 mL of acetonitrile. After stirring for 3 h, the green solution had turned burgundy and the solvent was removed to a trap under vacuum. The volatile fraction was subjected to GC analysis, which established the presence of 1,5-hexadiene; details are provided as Supporting Information. The burgundy residue was triturated with 3 × 5 mL of diethyl ether and the combined ether extracts were concentrated under vacuum to give the neutral chromium allyl complex **1** (6 mg, 47%), identified spectroscopically by comparison to authentic material.[6] The remaining purple residue was recrystallized from acetonitrile/diethyl ether at −35 °C to give [(η^5-C_5H_5)$Cr(NCCH_3)_3$]$(PF_6)_2$, **7** (14 mg, 43%), as determined by comparison of the infrared spectrum and combustion analysis to authentic material from independent synthesis, given below.

[(η^5-Cyclopentadienyl)tris(acetonitrile)chromium]-$(PF_6)_2$, 7, from [(η^5-C_5H_5)$CrCl_2$]$_2$. In a Schlenk flask under an inert atmosphere [(η^5-C_5H_5)$CrCl_2$]$_2$[4c] (50 mg, 0.133 mmol) was dissolved in 20 mL of acetonitrile. A solution of silver hexafluorophosphate (134 mg, 0.532 mmol) in 10 mL of acetonitrile was added. A white precipitate formed immediately, and the solution changed color from green to dark purple. The mixture was stirred for 2 h and filtered through a frit layered with Celite, and the filtrate was mixed with 15 mL of diethyl ether. After 2 days at −35 °C, deep purple crystals were deposited. The supernatant was removed and the crystals were washed with 2 × 10 mL of diethyl ether and dried to give the tris(acetonitrile) complex **7** (102 mg, 72%). IR (ν_{CN}, cm^{-1}, Nujol): 2325, 2296. Anal. Calcd for $C_{11}H_{14}CrN_3P_2F_{12}$: C, 24.92; H, 2.66; N, 7.93. Found: C, 25.42; H, 2.50; N, 7.71.[23]

(η^5-C_5H_5)$Cr(CO)_2$(η^2-2-allyl-1,3-dimesitylimidazolyl), 8. To a solution of (η^5-C_5H_5)$Cr(CO)_2(C_3H_5)$, **1** (17.6 mg, 0.082 mmol), in benzene was added 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes) (25 mg, 0.082 mmol) dissolved in a minimum of benzene. After standing for 3 h at room temperature, light red crystals had deposited. The supernatant was decanted and the crystals were washed with 2 × 5 mL of diethyl ether. Drying under vacuum gave the zwitterionic adduct **8** (41 mg, 89%). IR (ν_{CO}, cm^{-1}, acetone): 1845, 1757. ^1H NMR (500 MHz, acetone-d_6): δ 7.84 (s, 2H, NCHCHN); 7.22 (br s, 2H, H_{meta}); 7.16 (br s, 2H, H_{meta}); 3.86 (s, 5H, C_5H_5); 3.63 (dd, J = 15.0, 2.5 Hz, 1H, CH_2); 2.39 (s, 6H, CH_{3-para}); 2.26 (s, 6H, $CH_{3-ortho}$); 2.14 (s, 6H, $CH_{3-ortho}$); 1.69 (m, 1H, $H_{central}$); 1.44 (dd, J = 15.0, 11.5 Hz, 1H, CH_2); 1.32 (dd, J = 8.0, 2.0 Hz, 1H, H_{syn}); −0.19 (dd, J = 9.5, 2.0 Hz, 1H, H_{anti}). ^{13}C NMR (125 MHz, C_6D_6): δ 258.3 (CO); 258.1 (CO); 153.2 (N*C*N); 141.9 (C_{para}); 135.9 (C_{ortho}); 135.5 (C_{ortho}); 132.0 (C_{ipso}); 130.8 (C_{meta}); 130.5 (C_{meta}); 123.7 (N*CC*N); 85.9 (C_5H_5); 35.9 ($C_{methylene}$); 34.6 ($C_{central}$); 29.5 ($C_{terminal}$); 21.1 (CH_{3-para}); 18.1 ($CH_{3-ortho}$); 17.8 ($CH_{3-ortho}$). The given spectroscopic assignments were deduced from homo- and heterocorrelated NMR spectroscopy; details are provided as Supporting Information. Anal. Calcd for $C_{31}H_{34}CrN_2O_2$: C, 71.79; H, 5.40; N, 6.61. Found: C, 71.21; H, 5.22; N, 6.83. Crystals suitable for X-ray diffraction analysis were grown from an equimolar mixture of complex **1** and IMes in THF upon standing at RT for 12 h, providing complex **8** as the 0.5 THF solvate.

[(η^5-Cyclopentadienyl)bis(trimethylphosphine)-dicarbonylchromium]PF_6, 9. To a suspension of (η^5-C_5H_5)-$Cr(CO)_2(C_3H_5)$]PF_6·$(DME)_{0.5}$, **4** (111 mg, 0.275 mmol), in 20 mL of DME was added PMe_3 (577 μL, 1.0 M in THF, 0.577 mmol). The color of the mixture immediately turned from dark green to light green, and a light green precipitate formed. After 30 min the solid was collected on a frit, washed with 2 × 10 mL of diethyl ether, and dried to give complex **9** as a yellow-green powder (48 mg, 33%). IR (ν_{CO}, cm^{-1}, Nujol): 1959, 1885. ^1H NMR (400 MHz, acetone-d_6): δ 5.25 (t, J = 2.0 Hz, 5H, C_5H_5); 1.84 (2nd order m, 18 H, PMe_3). ^{31}P NMR (162 MHz, acetone-d_6): 52.94 (s, PMe_3); −138.03 (sept, J = 708.1 Hz, PF_6). ^{13}C NMR (100 MHz, acetone-d_6): δ 245.8 (t, J = 51.1 Hz, CO);

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[23] The composition and bond connectivity of tris(acetonitrile) complex **7** was confirmed by a preliminary X-ray crystal structure analysis, which was abandoned prior to final refinement.

91.0 (s, C_5H_5); 19.6 (dd, J = 15.6 2.0 Hz, PMe_3). Crystals suitable for X-ray diffraction were grown from acetone at −35 °C. Anal. Calcd for $C_{13}H_{23}CrO_2P_3F_6$: C, 29.9; H, 4.44. Found: C, 30.84; H, 4.29.

{(η^5-Cyclopentadienyl)[1,2-bis(diphenylphosphino)ethane]dicarbonylchromium}PF_6, 10. To a suspension of (η^5-C_5H_5)Cr(CO)$_2$(C_3H_5)]PF_6·(DME)$_{0.5}$, **4** (125 mg, 0.309 mmol), in 20 mL of DME was added dppe (117 mg, 0.294 mmol). The color of the mixture immediately turned from dark green to light green, and after 30 min the solvent was removed under vacuum. The residue was triturated with 2 × 10 mL of pentane and the remaining material dissolved in 10 mL of acetone. Diethyl ether (5 mL) was added and the solution was stored at −35 °C for 12 h to yield a yellow precipitate. The solid was collected on a frit, washed with 2 × 10 mL of diethyl ether, and dried to give complex **10** as a yellow powder (45 mg, 21%). IR (ν_{CO}, cm^{-1}, Nujol): 1971, 1917. ^{1}H NMR (500 MHz, acetone-d_6): δ 7.83 (m, 5H, Ph); 7.62 (m, 6H, Ph); 7.33 (m, 5H, Ph); 7.23 (m, 4H, Ph); 4.86 (t, J = 1.5 Hz, 5H, C_5H_5); 3.43 (2nd order m, 2H, CH_2); 3.12 (2nd order m, 2H, CH_2). ^{31}P NMR (162 MHz, acetone-d_6): 106.78 (s, dppe); −137.93 (sept, J = 708.1 Hz, PF_6). ^{13}C NMR (100 MHz, acetone-d_6): δ 249.0 (t, J = 28.7 Hz, CO); 137.6 (t, J = 24.6 Hz, C_{ipso}); 133.6 (t, J = 3.9 Hz, C_{meta}); 133.4 (t, J = 22.2 Hz, C_{ipso}); 132.2 (s, C_{para}); 132.1 (s, C_{para}); 131.5 (t, J = 3.9 Hz, C_{meta}); 130.4 (t, J = 5.1 C_{ortho}); 129.6 (t, J = 4.8 Hz, C_{ortho}); 93.2 (s, C_5H_5); 28.7 (dd, J = 39.8 Hz, CH_2CH_2). Anal. Calcd for $C_{33}H_{29}CrO_2P_3F_6$: C, 55.32; H, 4.08. Found: C, 55.14; H, 4.11. Crystals suitable for X-ray diffraction were grown from a 1:1 mixture of acetone and diethyl ether at −35 °C.

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Supporting Information Available: Parameters and measurements from the GC analysis; details of the two-dimensional NMR spectroscopy and assignments for complex **8**; details of the X-ray structure determinations for complexes **1**, **4**, **8**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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