Chromium Imidate Complexes from the Metathesis-Like Reaction of Phosphinimines and Chromium(0) Fischer Carbene Complexes

Israel Fernández, María José Mancheño,* Mar Gómez-Gallego, and Miguel A. Sierra*,†

Departamento de Química Orgánica, Facultad de Química, Universidad Complutense de Madrid, 28040 Madrid, Spain

Tore Lejon and Lars K. Hansen‡

Department of Chemistry, University of Tromsø, N-9037 Tromsø, Norway

Received December 4, 2003

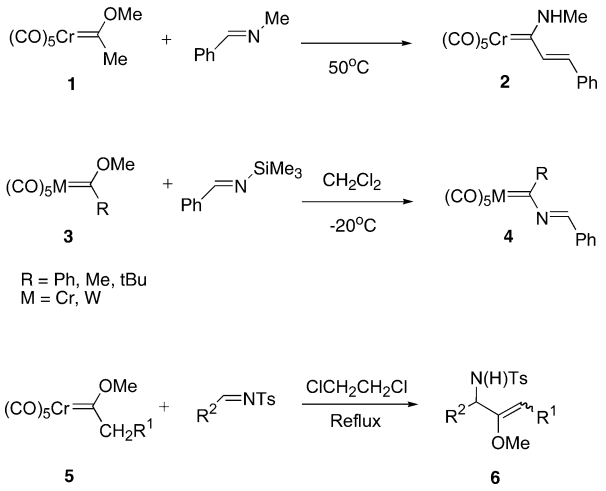
The thermal reaction of phosphinimines with alkyl-substituted chromium(0) Fischer carbene complexes is reported. The process occurs through a metathesis-like reaction to yield stable chromium imidate complexes. The formation of the azametallacycle **15** from zwitterion **14** is the key to the process. The length of the phosphinimine tether, the electrophilicity of the imine moiety, and the bulkiness of the imine substituents determine whether the metathesis process occurs. Only those compounds having short or rigid tethers and electrophilic and moderately hindered imine groups react with electrophilic Fischer carbene complexes. Bulkier imines or less electrophilic carbene complexes are unable to form the key azametallacycles and either decompose or form the condensation products derived from acid−base reactivity.

Introduction

The chemistry of Fischer carbene complexes has experienced a great development in the last few years, mainly due to their unique reactivity. Today many efficient processes are based on these versatile synthons, which have become very valuable building blocks in organic synthesis.[1] In this context, the reactivity of Fischer carbene complexes with imines has been a subject of interest, as imines have both nucleophilic and electrophilic sites and are unsaturated, a combination of factors that could lead to different reaction pathways.

The thermal behavior of group 6 Fischer carbene complexes toward imines is strongly dependent on the structure of the reagents and the reaction conditions. Thus, the reaction of the methyl complex **1** with the *N*-methyl imine of benzaldehyde gives the α,*β*-unsaturated complex **2** as a result of a base-induced condensation between the relatively acidic compound **1** and the imine.[2] On the other hand, imino complexes **4** can be obtained from acyloxy- and alkoxycarbene complexes **3** and *N*-trimethylsilyl imines.[3] Additionally, heating alkoxycarbene complexes **5** and *N*-tosylimines forms the *β*-methoxyallylamine derivatives **6**[4] (Scheme 1). The reactivity of imines, enamines, and azadienes with α,*β*-unsaturated group 6 carbene complexes has been thoroughly investigated by Barluenga's group, which has allowed them to describe a plethora of novel cycloaddition processes.[5] Finally, the photoinduced reaction of Fischer carbene complexes with imines to produce

Scheme 1



† E-mail: sierraor@quim.ucm.es.

‡ To whom inquiries regarding the structural determination of complex **10a** should be addressed.

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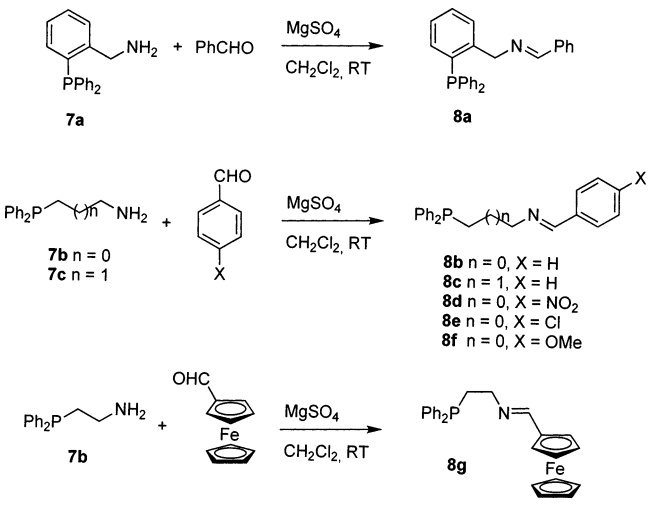
10.1021/om034347x CCC: $27.50
Publication on Web 03/20/2004

Scheme 2



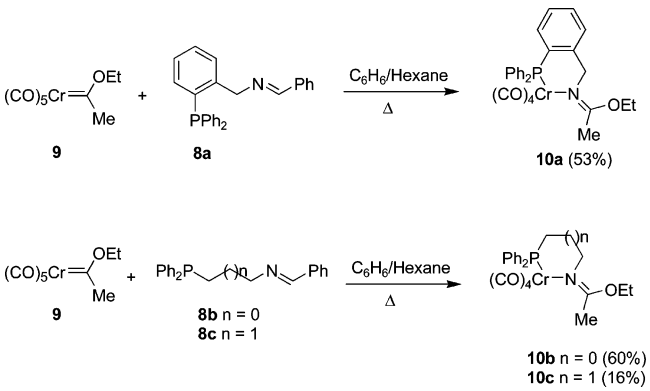
β-lactams has also been studied in depth. This reaction involves the reversible formation of chromium ketene complexes able to react with ketenophiles to yield ketene-derived products by either inter- or intramolecular reactions.[6] This type of process has been widely applied in synthesis[1d,6] and has been of longstanding mechanistic interest.[7]

The reaction of Fischer carbene complexes with phosphines is a well-known process that leads to new carbene complexes formed by ligand exchange of the coordination sphere of the metal.[8] During our studies directed at discovering novel processes in the chemistry of group 6 metal carbenes,[7b,c] the synthesis of chromium(0) carbene complexes having phosphinimine ligands was needed. Our results indicate that, instead of the expected CO−phosphine interchange, a new thermal process, the formation of imidate species coordinated to chromium, was observed. We report here a detailed study of the scope and limitations of this new type of reaction.

Results and Discussion

Imines **8** were prepared in quantitative yields from diphenylphosphino amines **7** and the corresponding aldehyde in CH_2Cl_2 at room temperature (Scheme 2). Heating equimolecular amounts of pentacarbonyl(ethoxymethylcarbene)chromium(0) (**9**) and imine **8a** in a mixture of hexane and benzene (1:1) yielded a new chromium complex lacking the carbene carbon (Scheme 3). The ^{13}C NMR spectrum of this complex exhibited three signals at 227.2, 227.0, and 219.0 ppm attributable to a $[(CO)_4Cr]$ moiety, together with a signal at 166.3 ppm that may correspond to a C═N bond. The ^1H NMR analysis showed the presence of a methyl group (δ 2.44 (s)) and an ethoxy group (δ 1.33 (t) and 4.05 (q)) linked to an sp^2 carbon. A single crystal of this compound was submitted to X-ray diffraction analysis, and its structure was unambiguously established as the cyclic phosphinoimidate $(CO)_4Cr$ complex **10a** (Figure 1).[9] The reaction of complex **9** with imines **8b**,**c** under the same conditions as those above produced the analogous complexes **10b**,**c** in 60% and 16% yields, respectively. In this latter case, together with complex **10c**, a new carbene complex was formed in 6% yield. This compound was identified as pentacarbonyl(ethoxystyrylcarbene)chromium(0), by comparison of its spectroscopic data with those obtained from an authentic sample.[10] In all

Scheme 3



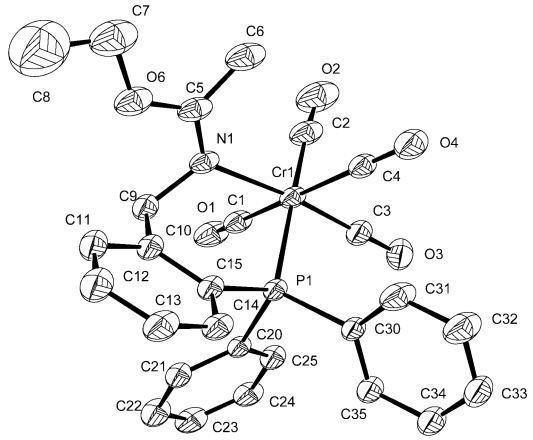


Figure 1. ORTEP drawing of complex **10a**. Hydrogens atoms have been omitted for clarity.

(5) For reactions of Fischer carbene complexes with α,β-unsaturated imines, see: (a) Danks, T. N.; Velo-Rego, D. *Tetrahedron Lett.* **1994**, *35*, 9443. (b) Barluenga, J.; Tomás, M.; Ballesteros, A.; Santamaría, J.; López-Ortíz, F. *J. Chem. Soc., Chem. Commun.* **1994**, 321. (c) Barluenga, J.; Tomás, M.; López-Pelegrín, J. A.; Rubio, E. *J. Chem. Soc., Chem. Commun.* **1995**, 665. (d) Barluenga, J.; Tomás, M.; Rubio, E.; López-Pelegrín, J. A.; García-Granda, S.; Pertierra, P. *J. Am. Chem. Soc.* **1996**, *118*, 695. (e) Barluenga, J.; Tomás, M.; Ballesteros, A.; Santamaría, J.; Carbajo, R. J.; López-Ortíz, F.; García-Granda, S.; Pertierra, P. *Chem. Eur. J.* **1996**, *2*, 88. (f) Barluenga, J.; Tomás, M.; Ballesteros, A.; Suárez-Sobrino, A. *J. Org. Chem.* **1997**, *62*, 9299. (g) Barluenga, J.; Tomás, M.; Rubio, E.; López-Pelegrín, J. A.; García-Granda, S.; Priede, M. P. *J. Am. Chem. Soc.* **1999**, *121*, 3065 and references therein. For other reactions, see: (h) Kagoshima, H.; Akiyama, T. *J. Am. Chem. Soc.* **2000**, *122*, 11741. (i) Kagoshima, H.; Okamura, T.; Akiyama, T. *J. Am. Chem. Soc.* **2001**, *123*, 7182.

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(8) Fischer, E. O.; Fischer, H. *Chem. Ber.* **1974**, *107*, 657.

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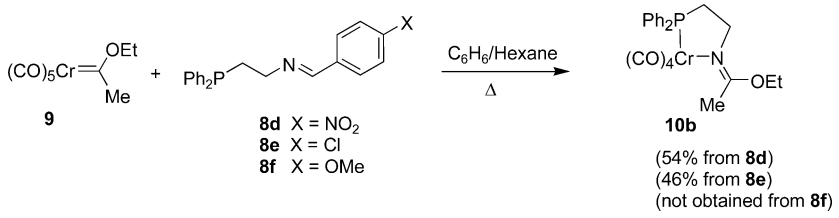
(10) Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537.

Scheme 4

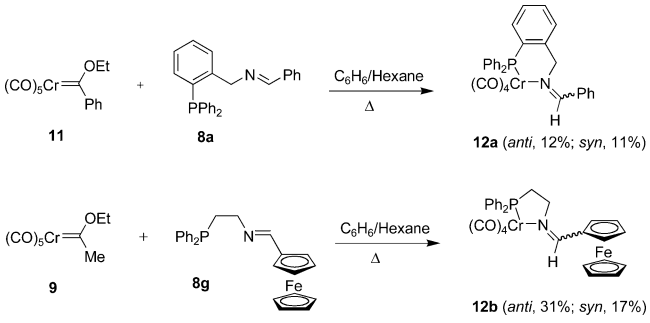


cases, the imidate complexes **10** were obtained as single isomers and their structures were established by comparison with the spectroscopic data of **10a**.

To evaluate the role of the electrophilicity of the C═N double bond in the formation of the imidate complexes, the reactions of complex **9** with imines **8d**−**f** having electron-withdrawing or electron-donating groups in the aromatic ring were tested next. The results are compiled in Scheme 4. The most electrophilic imine, **8d**, yielded complex **10b** in 54% yield. Imine **8e** behaves in a similar way, affording complex **10b** in 46% yield, but the less electrophilic imine **8f** rendered a complex reaction mixture where pentacarbonyl[ethoxy(*p*-methoxystyryl)carbene]chromium(0) was the only product that could be isolated (Scheme 4).

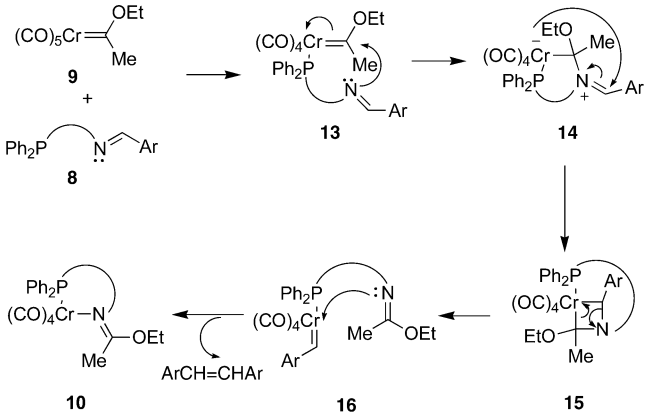
The reactivity of ethoxyphenyl chromium carbene complex **11** with imine **8a** was tested next. This time, the imino complex **12a** was the sole identifiable reaction product and was obtained as a syn/anti mixture of isomers across the double bond. The isomers were separated by column chromatography on silica gel, and their structures were established on the basis of NOE measurements. A similar behavior was found when complex **9** was treated with the bulky ferrocenylimine **8g**, yielding a syn/anti mixture of ferrocenylimino complexes **12b** as reaction products. As in the case of **12a**, the isomers were separated by chromatography and their structures established on the basis of NOE measurements (Scheme 5).

Scheme 5



Clear trends emerge from the data above: the formation of chromium(0) imidate complexes **10** from the alkyl Fischer carbene complex **9** is favored with electrophilic phosphinimines **8**, while a less electrophilic carbene complex such as **11** or a bulky substituent at the imine carbon (as in **8g**) leads exclusively to products **12**, in which the carbene and one of the CO ligands have been interchanged by the phosphinimine moiety. Considering all the experimental observations, the formation of imidate complexes **10** could be explained by a stepwise mechanism, which is illustrated in Scheme 6. The thermal CO−phosphine ligand exchange should form intermediate **13** in the first step. Nucleophilic attack of the imine moiety on the electrophilic carbene carbon may lead to zwitterion **14**, which evolves to azametallacycle **15** by attack of the nucleophilic chromium center at the iminium moiety. Finally, breakage of the metallacyclic intermediate **15** should form the new carbene complex **16**, which evolves by extrusion of the arylcarbene moiety to compounds **10**.[11] This step may be induced by the metal−imidate coordination. Overall, the evolution of phosphinimines **8** to complexed imidates **10** can be considered a metathesis-like reaction (Scheme 6).

Scheme 6



The effect of the length of the tether on the yields of imidate complexes **10** (60% for imine **8b** and 16% for imine **8c**) and that of the rigidity (53% yield for imine **8a** and only 16% for imine **8c**) supports the hypothesis that the coordination of the phosphine ligand should precede the metallacycle formation. Otherwise, the reactivity of imines **8a**−**c** should be comparable. As the formation of metallacycle **15** requires the attack of the chromium nucleus at the C═N bond, poorly electrophilic imines inhibit this reaction step, leading to decomposition products together with compounds derived from the normal acid−base reactivity reported earlier by Hegedus.[2] Other factors disfavoring the formation of this key intermediate **15** are bulky substituents on the imine (as in **8g**) or the choice of a less reactive Fischer carbene complex, such as **11**.

(11) The detection of mixtures of *cis*- and *trans*-stilbenes in the reaction of acyloxy- and alkoxycarbene complexes and *N*-trimethylsilyl imines has been reported by Wulff.[3] We have carried out the reactions of complex **9** and imines **8b**,**d** with the goal of isolating the expected products of evolution of the corresponding intermediates **16**. Direct observation of stilbenes was hampered due to the presence of the diphenylphosphine moiety, which masked the aromatic region of the NMR spectra of the crude reaction mixtures. Chromatography led to pure imidate complex **10b**, together with mixtures of unidentified products. The sequence irradiation−light oxidation was used also in these reactions, leading to total decomposition of complex **10b** together with very complex reaction mixtures.

Finally, to check the effect of the metal in the starting carbene on the reaction mechanism, imine **8a** was treated with pentacarbonyl(ethoxymethylcarbene)tungsten(0) under the same conditions used for complex **9**. In this case, the expected imidate was not formed and the reaction yielded a complex mixture of products from which only pentacarbonyl(ethoxystyrylcarbene)tungsten(0) could be isolated. This result may be explained by the lower electrophilicity of the carbene carbon in tungsten Fischer carbene complexes, compared to their chromium analogues, which is further diminished in this case by the electron-donating effect of the phosphine ligand.

In summary, a new thermal reaction of imines with chromium Fischer carbene complexes has been studied. Stable chromium imidate complexes are obtained in a metathesis-like process.[12,13] The formation of azametallacycles **15** from zwitterions **14** is the key to the reaction. The length of the phosphinimine tether, the electrophilicity of the C=N bond, and the bulkiness of the imine substituents determine whether the metathesis-like process occurs. Only those compounds having short or rigid tethers or electrophilic and moderately hindered C=N groups react with electrophilic carbene complexes. Otherwise, bulkier imines or less electrophilic carbene complexes are unable to form the key azametallacycles and either decompose or form the condensation products derived from acid−base reactivity.

Experimental Section

General Procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded at 22 °C on Bruker Avance 300 (300.1 and 75.4 MHz) or Bruker 200-AC (200.1 and 50 MHz) spectrometers. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm) and $CDCl_3$ (^{13}C, 77.0 ppm). IR spectra were taken on a Perkin-Elmer 781 spectrometer. Flame-dried glassware and standard Schlenk techniques were used for moisture-sensitive reactions. Merck silica gel (230−400 mesh) was used as the stationary phase for purification of crude reaction mixtures by flash column chromatography. Identification of products was made by TLC (Kieselgel 60F-254). UV light (λ 254 nm) and 5% phosphomolybdic acid solution in 95% EtOH were used to develop the plates.

All commercially available compounds were used without further purification. 2-(Diphenylphosphino)benzylamine was prepared according to literature methods.[14]

General Procedure for the Synthesis of Phosphinimines 8a−g. A solution of 2-(diphenylphosphino)ethylamine, 3-(diphenylphosphino)propylamine, or 2-(diphenyphosphino)-benzylamine and the corresponding benzaldehyde in stoichiometric amounts and a large excess of $MgSO_4$ in dry CH_2Cl_2 were stirred at room temperature for 24 h. The mixture was filtered, and the solvent was removed under reduced pressure to yield the corresponding imines.

Imine 8a. Following the general procedure, from 570 mg (1.96 mmol) of 2-(diphenylphosphino)benzylamine (**7a**), 208 mg (1.96 mmol) of benzaldehyde, 1.77 g (14.7 mmol) of $MgSO_4$, and 30 mL of dry Et_2O was obtained 742 mg (quantitative yield) of the imine **8a** as a pale pink oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.97 (s, 2H), 6.82 (m, 2H), 7.18−7.51 (m, 18H), 8.16 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 63.0 (d, $J_{C-P} = 22.7$ Hz), 127.1, 128.1, 128.4 (d, $J_{C-P} = 3.5$ Hz), 128.6 (d, $J_{C-P} = 2.8$ Hz), 129.0, 130.5, 132.0 (d, $J_{C-P} = 9.6$ Hz), 133.4, 133.9 (d, $J_{C-P} = 19.9$ Hz), 136.3 (d, $J_{C-P} = 20.2$ Hz), 136.4, 143.9 (d, $J_{C-P} = 24.1$ Hz), 162.3. IR (CCl_4): ν 3057, 2926, 2854, 1647, 1435 cm^{-1}. Anal. Calcd for $C_{26}H_{22}NP$: C, 82.30; H, 5.84; N, 3.69. Found: C, 82.51; H, 5.69; N, 3.84.

Imine 8b. Following the general procedure, from 500 mg (2.18 mmol) of 2-(diphenylphosphino)ethylamine (**7b**), 213 mg (2.18 mmol) of benzaldehyde, 1.97 g (16.4 mmol) of $MgSO_4$, and 35 mL of dry CH_2Cl_2 was obtained 692 mg (quantitative yield) of the imine **8b** as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.41 (m, 2H), 3.06 (m, 2H), 7.24−7.40 (m, 13H), 7.58 (m, 2H), 8.15 (s, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 29.8 (d, $J_{C-P} = 12.7$ Hz), 58.4 (d, $J_{C-P} = 21.1$ Hz), 128.0, 128.5, 128.5 (d, $J_{C-P} = 8.0$ Hz), 128.7, 130.6, 132.7 (d, $J_{C-P} = 18.8$ Hz), 136.0, 138.3 (d, $J_{C-P} = 12.4$ Hz), 161.3. IR (CCl_4): ν 3057, 2841, 1643, 1433 cm^{-1}. Anal. Calcd for $C_{21}H_{20}NP$: C, 79.47; H, 6.35; N, 4.41. Found: C, 79.62; H, 6.21; N, 4.65.

Imine 8c. Following the general procedure, from 323 mg (1.33 mmol) of 2-(diphenylphosphino)propylamine (**7c**), 141 mg (1.33 mmol) of benzaldehyde, 1.20 g (9.96 mmol) of $MgSO_4$, and 25 mL of dry CH_2Cl_2 was obtained, after vacuum distillation, 410 mg (93%) of the imine **8c** as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1,81 (m, 2H), 2.05 (m, 2H), 3.67 (td, 2H, $J = 6.7$ Hz, $J_{H-P} = 0.9$ Hz), 7.23−7.37 (m, 13H), 7.63 (m, 2H), 8.19 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 25.6 (d, $J_{C-P} = 11.7$ Hz), 27.3 (d, $J_{C-P} = 16.3$ Hz), 64.2 (d, $J_{C-P} = 13.1$ Hz), 128.0, 128.4 (d, $J_{C-P} = 8.9$ Hz), 128.4, 128.5, 130.5, 132.7 (d, $J_{C-P} = 18.4$ Hz), 136.2, 138.6 (d, $J_{C-P} = 13.1$ Hz), 161.2. IR (CCl_4): ν 3059, 2926, 2852, 1708, 1647, 1435 cm^{-1}. Anal. Calcd for $C_{22}H_{22}NP$: C, 79.74; H, 6.69; N, 4.23. Found: C, 79.55; H, 6.84; N, 4.50.

Imine 8d. Following the general procedure, from 248 mg (1.08 mmol) of 2-(diphenylphosphino)ethylamine (**7b**), 163 mg (1.08 mmol) of *p*-nitrobenzaldehyde, 977 mg (8.11 mmol) of $MgSO_4$, and 18 mL of dry CH_2Cl_2 were obtained 391 mg (quantitative yield) of the imine **8d** as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.39 (m, 2H), 3.70 (m, 2H), 7.19−7.37 (m, 10H), 7.65 (d, 2H, $J = 8.8$ Hz), 8.07 (d, 2H, $J = 8.8$ Hz), 8.14 (s, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 29.4 (d, $J_{C-P} = 13.1$ Hz), 58.5 (d, $J_{C-P} = 20.3$ Hz), 123.5, 128.2 (d, $J_{C-P} = 6.9$ Hz), 128.4, 128.5, 132.6 (d, $J_{C-P} = 18.7$ Hz), 138.0 (d, $J_{C-P} = 12.4$ Hz), 141.3, 148.7, 158.8. IR (CCl_4): ν 3057, 2922, 2850, 1647, 1603, 1525, 1435, 1344 cm^{-1}. Anal. Calcd for $C_{21}H_{19}N_2O_2P$: C, 69.61; H, 5.29; N, 7.73. Found: C, 69.84; H, 5.14; N, 7.94.

Imine 8e. Following the general procedure, from 150 mg (0.65 mmol) of 2-(diphenylphosphino)ethylamine (**7b**), 92 mg

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(0.96 mmol) of *p*-chlorobenzaldehyde, 591 mg (4.9 mmol) of $MgSO_4$, and 11 mL of dry CH_2Cl_2 was obtained 230 mg (quantitative yield) of imine **8e** as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (m, 2H), 3.62 (m, 2H), 7.18−7.67 (m, 14H), 8.02 (s, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 29.6 (d, J_{C-P} = 12.5 Hz), 58.3 (d, J_{C-P} = 20.8 Hz), 128.3 (d, J_{C-P} = 6.8 Hz), 128.5, 128.6, 129.1, 132.6 (d, J_{C-P} = 18.8 Hz), 134.4, 136.4, 138.2 (d, J_{C-P} = 12.4 Hz), 159.8. IR (CCl_4): ν 3057, 2925, 2852, 1645, 1489, 1458 cm^{-1}. Anal. Calcd for $C_{21}H_{19}ClNP$: C, 71.69; H, 5.44, N, 3.98; Found: C, 71.84; H, 5.51; N, 4.12.

Imine 8f. Following the general procedure, from 250 mg (1.09 mmol) of 2-(diphenylphosphino)ethylamine (**7b**), 149 mg (1.09 mmol) of anisaldehyde, 985 mg (8.2 mmol) of $MgSO_4$, and 18 mL of dry CH_2Cl_2 was obtained 379 mg (quantitative yield) of the imine **8f** as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.81 (m, 2H), 3.82 (s, 3H), 3.91 (m, 2H), 6.90−7.76 (m, 14H), 8.10 (s, 1H). ^{13}C NMR (50.0 MHz, $CDCl_3$): δ 29.9 (d, J_{C-P} = 12.8 Hz), 55.3, 58.1 (d, J_{C-P} = 20.2 Hz), 113.9, 128.3, 128.5 (d, J_{C-P} = 4.3 Hz), 128.7, 129.8, 132.7 (d, J_{C-P} = 18.8 Hz), 138.3 (d, J_{C-P} = 12.4 Hz), 160.5, 161.7. IR (CCl_4): ν 3057, 2918, 2837, 1647, 1433, 1250 cm^{-1}. Anal. Calcd for $C_{22}H_{22}$-NOP: C, 76.06; H, 6.38; N, 4.03. Found: C, 76.26; H, 6.47; N, 3.94.

Imine 8g. Following the general procedure, from 178 mg (0.78 mmol) of 2-(diphenylphosphino)ethylamine (**7b**), 167 mg (0.78 mmol) of ferrocenecarbaldehyde, 701 mg (5.8 mmol) of $MgSO_4$, and 15 mL of dry CH_2Cl_2 was obtained 331 mg (quantitative yield) of the imine **8g** as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.34 (m, 2H), 3.48 (m, 2H), 4.08 (s, 5H), 4.27 (s, 2H), 4.46 (s, 2H), 7.24−7.70 (m, 10H), 8.00 (s, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 29.9 (d, J_{C-P} = 12.6 Hz), 58.6 (d, J_{C-P} = 21.2 Hz), 68.4, 69.0, 70.3, 80.3, 128.4 (d, J_{C-P} = 6.7 Hz), 132.7 (d, J_{C-P} = 18.6 Hz), 138.4 (d, J_{C-P} = 12.5 Hz), 161.4. IR (CCl_4): ν 3057, 2923, 2852, 1645 cm^{-1}. Anal. Calcd for $C_{25}H_{24}$-FeNP: C, 70.60; H, 5.69, N, 3.29. Found: C, 70.41; H, 5.81; N, 3.08.

General Procedure for the Synthesis of Phosphine Imidate Complexes 10. A solution of the metal carbene complex and the corresponding phosphinimine in degassed hexane−benzene (1:1) was heated at reflux for 9 h (unless otherwise specified). The solvents were removed under reduced pressure, and the residue was submitted to flash column chromatography (SiO_2, hexane−AcOEt) under an argon atmosphere to give pure compounds.

Complex 10a. Following the general procedure, from 517 mg (1.96 mmol) of complex **9**[15] and 742 mg (1.96 mmol) of imine **8a** in 30 mL of hexane−benzene (1:1) was obtained after purification by flash column chromatography 549 mg (53%) of complex **10a** as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (t, 3H, J = 7.0 Hz), 2.44 (s, 3H), 4.05 (q, 2H, J = 7.0 Hz), 4.36 (d, 2H, J = 3.3 Hz), 6.89 (t, 1H, J = 1.1 Hz), 7.22−7.41 (m, 13H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.9, 20.0, 58.4 (d, J_{C-P} = 13.9 Hz), 66.0, 128.3 (d, J_{C-P} = 9.1 Hz), 128.5, 129.6, 130.1, 130.5 (d, J_{C-P} = 7.5 Hz), 132.8, 132.9 (d, J_{C-P} = 11.0 Hz), 134.9 (d, J_{C-P} = 35.7 Hz), 143.2 (d, J_{C-P} = 17.5 Hz), 166.3, 219.0 (d, J_{C-P} = 12.3 Hz), 227.0 (d, J_{C-P} = 1.9 Hz), 227.2 (d, J_{C-P} = 14.7 Hz). IR (KBr): ν 2009, 1900, 1886, 1852 cm^{-1}. Anal. Calcd for $C_{27}H_{24}CrNO_5P$: C, 61.72; H, 4.60, N, 2.67. Found: C, 61.95; H, 4.48; N, 2.49.

Phosphine Imidate Complex 10b. Compound **10b** was obtained by reaction of Fischer carbene complex **9** with imines **8b**,**d,e** as specified below.

(a) From Imine 8b. Following the general procedure, from 278 mg (1.05 mmol) of complex **9** and 335 mg (1.05 mmol) of imine **8b** in 20 mL of hexane−benzene (1:1), complex **10b** (294 mg, 60%) was obtained as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (t, 3H, J = 7.0 Hz), 2.25 (m, 2H), 2.45 (s, 3H), 3.53 (m, 1H), 3.61 (m, 1H), 4.03 (q, 2H, J = 7.0 Hz), 7.32−7.38 (m, 6H), 7.55−7.63 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.7, 20.7, 29.0 (d, J_{C-P} = 16.8 Hz), 48.2 (d, J_{C-P} = 9.4 Hz), 65.8, 128.5 (d, J_{C-P} = 9.1 Hz), 129.6 (d, J_{C-P} = 0.7 Hz), 131.5 (d, J_{C-P} = 11.1 Hz), 136.7 (d, J_{C-P} = 34.7 Hz), 165.8 (d, J_{C-P} = 2.3 Hz), 219.2 (d, J_{C-P} = 14.3 Hz), 227.8 (d, J_{C-P} = 2.0 Hz), 229.1 (d, J_{C-P} = 14.7 Hz). IR (KBr): ν 2004, 1871, 1834, 1624 cm^{-1}. Anal. Calcd for $C_{22}H_{22}CrNO_5P$: C, 57.02; H, 4.79; N, 3.02. Found: C, 56.87; H, 4.90; N, 3.21.

(b) From Imine 8d. Following the general procedure, from 137 mg (0.52 mmol) of complex **9** and 188 mg (0.52 mmol) of imine **8d** in 9 mL of hexane−benzene (1:1), complex **10b (**131 mg, 54%) was obtained as an orange solid.

(c) From Imine 8e. Following the general procedure, from 173 mg (0.65 mmol) of complex **9** and 230 mg (0.65 mmol) of imine **8e** in 12 mL of hexane−benzene (1:1), complex **10b** (139 mg, 46%) was obtained after purification by flash column chromatography on silica gel.

Complex 10c. Following the general procedure, from 526 mg (1.99 mmol) of complex **9** and 660 mg (1.99 mmol) of imine **8c** in 30 mL of hexane−benzene (1:1), complex **10c** (148 mg, 16%) was obtained as an orange solid together with 40 mg (6%) of pentacarbonyl(ethoxystyrylcarbene)chromium(0).[10] ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (t, 3H, J = 7.0 Hz), 1.50 (m, 2H), 2.29 (m, 2H), 2.43 (s,3H), 3.33 (m, 2H), 4.01 (q, 2H, J = 7.0 Hz), 7.31−7.45 (m, 10H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.4, 23.6, 23.6, 29.6 (d, J_{C-P} = 20.2 Hz), 40.4 (d, J_{C-P} = 14.7 Hz), 65.9, 128.4 (d, J_{C-P} = 8.6 Hz), 129.6 (d, J_{C-P} = 1.8 Hz), 131.7 (d, J_{C-P} = 10.4 Hz), 136.9 (d, J_{C-P} = 31.9 Hz), 167.2, 221.3 (d, J_{C-P} = 14.7 Hz), 225.6 (d, J_{C-P} = 5.5 Hz), 230.8 (d, J_{C-P} = 12.9 Hz). IR (CCl_4): ν 2008, 1925, 1890 cm^{-1}. Anal. Calcd for C_{23}-$H_{24}CrNO_5P$: C, 57.86; H, 5.07; N, 2.93. Found: C, 57.62; H, 5.18; N, 3.09.

Complex 12a. Following the general procedure, from 344 mg (1.05 mmol) of complex **11**[16] and 300 mg (0.48 mmol) of imine **8a** in 20 mL of hexane−benzene (1:1) and after chromatography on silica gel, 71 mg (12%) of *anti*-**12a** and 65 mg (11%) of *syn*-**12a** were obtained as orange solids. Complex **12a** (anti isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.60 (s, 2H), 6.74 (m, 1H), 6.88 (m, 2H), 7.09−7.41 (m, 16H), 9.05 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 62.6 (d, J_{C-P} = 9.7 Hz), 127.3, 128.5 (d, J_{C-P} = 9.1 Hz), 128.8, 129.0 (d, J_{C-P} = 4.5 Hz), 129.8, 130.1, 130.3, 130.7, 131.1, 132.7, 133.0 (d, J_{C-P} = 11.3 Hz), 134.5 (d, J_{C-P} = 36.0 Hz), 141.5 (d, J_{C-P} = 17.5 Hz), 172.4 (d, J_{C-P} = 4.2 Hz), 219.6 (d, J_{C-P} = 12.8 Hz), 225.9, 227.3 (d, J_{C-P} = 13.9 Hz); IR (KBr) ν 2006, 1882, 1846 cm^{-1}. Anal. Calcd for $C_{30}H_{22}$-$CrNO_4P$: C, 66.30; H, 4.08; N, 2.58. Found: C, 66.51; H, 4.21; N, 2.71. Complex **12a** (syn isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.80 (d, 2H, J = 2.3 Hz), 6.93 (m, 1H), 7.21−7.42 (m, 18H), 8.80 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 76.3 (d, J_{C-P} = 12.5 Hz), 128.1, 128.4, 128.5 (d, J_{C-P} = 9.2 Hz), 129.2 (d, J_{C-P} = 3.7 Hz), 129.8, 130.4, 130.8, 130.9, 132.3, 133.0 (d, J_{C-P} = 11.1 Hz), 134.4 (d, J_{C-P} = 36.0 Hz), 136.2, 141.9 (d, J_{C-P} = 18.2 Hz), 174.5 (d, J_{C-P} = 2.1 Hz), 219.1 (d, J_{C-P} = 12.7 Hz), 224.5 (d, J_{C-P} = 1.8 Hz), 227.6 (d, J_{C-P} = 14.5 Hz); IR (KBr) ν 2004, 1880, 1844 cm^{-1}. Anal. Calcd for $C_{30}H_{22}$-$CrNO_4P$: C, 66.30; H, 4.08; N, 2.58. Found: C, 66.44; H, 4.23; N, 2.63.

Complex 12b. Following the general procedure, from 205 mg (0.78 mmol) of complex **9** and 330 mg (0.78 mmol) of imine **8g** in 13 mL of hexane−benzene (1:1) and after chromatography on silica gel, 142 mg (31%) of *anti*-**12b** and 79 mg (17%) of *syn*-**12b** were obtained as orange solids. Complex **12b** (anti isomer): ^{1}H NMR (300 MHz, acetone-d_6) δ 2.66 (m, 2H), 3.63 (m, 1H), 3.71 (m, 1H), 4.20 (s, 5H), 4.50 (t, 2H, J = 1.9 Hz), 4.71 (t, 2H, J = 1.9 Hz), 7.33−7.38 (m,6H), 7.66−7.73 (m, 4H), 8.61 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 30.7 (d, J_{C-P} = 16.7 Hz), 53.7 (d, J_{C-P} = 8.3 Hz), 69.7, 71.4, 72.2, 76.6, 128.7 (d, J_{C-P} = 9.1 Hz), 129.8, 131.6 (d, J_{C-P} = 11.6 Hz), 136.0 (d,

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J_{C-P} = 34.3 Hz), 168.9, 219.9 (d, J_{C-P} = 14.1 Hz), 227.4, 229.3 (d, J_{C-P} = 12.9 Hz); IR (KBr) ν 2002, 1877, 1830, 1608 cm^{-1}. Anal. Calcd for $C_{29}H_{24}CrFeNO_4P$: C, 59.10; H, 4.10; N, 2.38. Found: C, 59.26; H, 3.95; N, 2.51. Complex **12b** (syn isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 2.45 (m, 2H), 3.71 (m, 1H), 3.80 (m, 1H), 4.13 (s, 5H), 4.52 (t, 2H, J = 1.9 Hz), 5.03 (t, 2H, J = 1.9 Hz), 7.35−7.37 (m, 6H), 7.58−7.64 (m, 4H), 8.40 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 29.6 (d, J_{C-P} = 16.2 Hz), 68.5 (d, J_{C-P} = 8.3 Hz), 69.8, 72.1, 72.2, 76.9, 128.7 (d, J_{C-P} = 8.8 Hz), 129.8 (d, J_{C-P} = 1.6 Hz), 131.5 (d, J_{C-P} = 11.1 Hz), 136.4 (d, J_{C-P} = 35.2 Hz), 171.7, 219.4 (d, J_{C-P} = 14.3 Hz), 227.3 (d, J_{C-P} = 2.7 Hz), 229.1 (d, J_{C-P} = 14.3 Hz); IR (KBr) ν 2004, 1878, 1834, 1618 cm^{-1}. Anal. Calcd for $C_{29}H_{24}CrFeNO_4P$: C, 59.10; H, 4.10; N, 2.38. Found: C, 59.01; H, 3.98; N, 2.43.

Acknowledgment. Financial support by the Spanish Ministerio de Ciencia y Tecnología (Grant BQU2001-1283) and the Comunidad Autónoma de Madrid (Grant 07M/0043/2002) is gratefully acknowledged. I.F. thanks the Ministerio de Eduación y Ciencia (Spain) for a predoctoral fellowship.

Supporting Information Available: Tables giving X-ray characterization data for compound **10a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034347X