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A Simple Approach toward Enantiomerically Pure Fischer Carbene Complexes of Chromium and Molybdenum: Chiral Modification of the Metal Fragment

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Replacing two carbonyl ligands of the common pentacarbonyl fragment by the suitable chiral biphosphite ligand **2** allows for the novel synthesis of stable chiral Fischer carbene complexes of molybdenum and chromium. In the case of the phenyl molybdenum complex **1**, this exchange reaction yields complex *fac*-**3**, which can be thermally isomerized to *mer*-**3**. The thermal reaction exchange of methyl, phenyl, and alkenyl chromium carbene complexes **4a**−**c** with ligand **2** affords directly the complexes *mer*-**5a**−**c**. Two of the novel complexes, *fac*-**3** and *mer*-**5a**, have been characterized in the solid state.

Introduction

The influence of transition-metal compounds on synthetic organic chemistry has experienced a significant increase in recent years,[1] and transition-metal carbene complexes have been among the most fascinating of such structures.[2] Among the vast number of different carbene complexes, Fischer type compounds of group 6 metals are of major synthetic importance.[3] In recent years, their unique structure has been the basis for both the discovery of several novel reactions and the isolation of important reaction intermediates.[4,5]

Owing to this enormous potential of Fischer carbene complexes, there has been an increased interest in the synthesis of enantiomerically pure complexes for application in stoichiometric asymmetric processes.[3b,6] Generally, three different approaches can be devised for the chiral functionalization of alkoxy- and aminocarbene metal complexes. First, chiral derivatives can be introduced at the heteroatom position. Thus, chiral alcohols and amines have been employed in a broad variety of enantio- and diastereoselective reactions.[7,8] Incorporation of an organic skeleton from either chiral pool derivatives[9] or chiral synthetic precursors[10] is the second possibility, which, under expected substrate

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(1) *Transition Metals For Organic Chemistry: Building Blocks and Fine Chemicals*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 1998.

(2) (a) Zaragoza-Dörwald, F. *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 1999. (b) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; VCH: Weinheim, Germany, 1983.

(3) For recent reviews, see: (a) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 12, p 469. (b) Barluenga, J.; Flórez, J.; Fañanas, F. J. *J. Organomet. Chem.* **2001**, *624*, 5. (c) de Meijere, A.; Schirmer, H.; Duetsch, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3964. (d) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591. (e) Aumann, R. *Eur. J. Org. Chem.* **2000**, 17. (f) Herndon, J. W. *Tetrahedron* **2000**, *56*, 1257.

(4) For selected recent contributions in this area, see for instance: (a) Bao, J.; Wulff, W. D.; Dominy, J. B.; Fumo, M. J.; Grant, E. B.; Rob, A. C.; Whitcomb, M. C.; Yeung, S.-M.; Ostrander, R. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 3392. (b) Kagoshima, H.; Okamura, T.; Akiyama, T. *J. Am. Chem. Soc.* **2001**, *123*, 7182. (c) Iwasawa, N.; Shido, M.; Kusama, H. *J. Am. Chem. Soc.* **2001**, *123*, 5814. (d) Miura, T.; Iwasawa, N. *J. Am. Chem. Soc.* **2002**, *124*, 518.

(5) Selected recent contributions from our laboratory: (a) Barluenga, J.; López, L. A.; Löber, O.; Tomás, M.; García-Granda, S.; Alvarez-Rúa, C.; Borge, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3392. (b) Barluenga, J.; Aznar, F.; Palomero, M. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 4346. (c) Barluenga, J.; Aznar, A.; Gutiérrez, I.; Martín, A.; García-Granda, S.; Llorca-Baragaño, M. A. *J. Am. Chem. Soc.* **2000**, *122*, 1314. (d) Barluenga, J.; Rodríguez, F.; Fañanás, F. J.; Rubio, E. *Angew. Chem., Int. Ed.* **1999**, *38*, 3084. (e) Barluenga, J.; Ballesteros, A.; Santamaría, J.; Bernardo de la Rúa, R.; Rubio, E.; Tomás, M. *J. Am. Chem. Soc.* **2000**, *122*, 12874.

(6) (a) Wulff, W. D. *Organometallics* **1998**, *17*, 3116. (b) Dötz, K. H.; Tomuschat, P. *Chem. Soc. Rev.* **1999**, *28*, 187.

(7) (a) Barluenga, J.; Montserrat, J. M.; Flórez, J.; García-Granda, S.; Martín, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1392. (b) Rahm, A.; Rheingold, A. L.; Wulff, W. D. *Tetrahedron* **2000**, *56*, 4951. (c) Hsung, R. P.; Wulff, W. D.; Chamberlin, S.; Liu, Y.; Liu, R.-Y.; Wang, H.; Quinn, J. F.; Wang, S. L. B.; Rheingold, A. L. *Synthesis* **2001**, 200. (d) Barluenga, J.; Fernández-Rodríguez, M. A.; Aguilar, E.; Fernández-Marí, F.; Salinas, A.; Olano, B. *Chem. Eur. J.* **2001**, *7*, 3533. (e) Merino, I.; Laxmi, S.; Flórez, J.; Barluenga, J.; Ezquerra, J.; Pedregal, C. *J. Org. Chem.* **2002**, *67*, 648. (f) Dötz, K. H.; Stinner, C.; Nieger, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2535. (g) Hegedus, L. S.; Schwindt, M. A.; De Lombaert, S.; Imwinkelried, R. *J. Am. Chem. Soc.* **1990**, *112*, 2264. (h) Licandro, E.; Maiorana, S.; Capella, L.; Manzotti, R.; Papagni, A.; Vandoni, B.; Albinati, A.; Chuang, S. H.; Hwu, J.-R. *Organometallics* **2001**, *20*, 485.

(8) For chiral boroxycarbene complexes, see: (a) Barluenga, J.; Rodríguez, F.; Vadecard, J.; Bendix, M.; Fañanás, F. J.; López-Ortiz, F.; Rodríguez, M. A. *J. Am. Chem. Soc.* **1999**, *121*, 8776. (b) Barluenga, J.; Fañanás, F. J. *Tetrahedron* **2000**, *56*, 4597.

(9) (a) Janes, E.; Dötz, K. H.; *J. Organomet. Chem.* **2001**, *622*, 251. (b) Dötz, K. H.; Jäkel, C.; Haase, W.-C. *J. Organomet. Chem.* **2001**, *617*−*618*, 119. (c) Dötz, K. H.; Ehlenz, R. *Chem. Eur. J.* **1997**, *3*, 1751.

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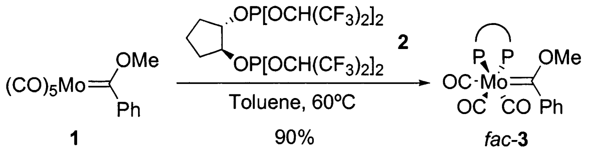
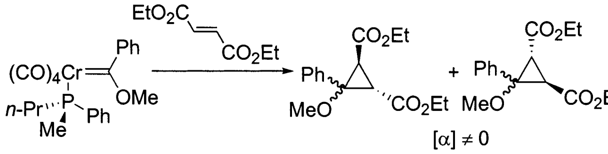
Scheme 1



control, will directly lead to modification of the organic group in a diastereoselective manner. There exists a third route that consists of a chiral modification of the metal coordination sphere itself. Surprisingly, this approach has encountered far less attention, though it apparently appears highly promising, especially in those reactions leading to metal-free products. Therefore, use of a chiral metal fragment would allow for the direct synthesis of enantiomerically pure organic molecules without the need of additional removal of the chiral auxiliary. It is interesting to note that such an approach had already been used by Fischer in an asymmetric cyclopropanation reaction.[11] Here, exchange of a CO ligand for an enantiopure electron-rich monophosphine yielded the corresponding chromium tetracarbonyl complex as a cis/trans mixture (eq 1). An optically active mixture of cyclopropanes was obtained from reaction with diethyl fumarate, although a detailed discussion on its stereochemical course was omitted.



(1)

Results and Discussion

We now describe the first examples of Fischer carbene complexes of group 6 transition metals in which two of the original carbonyl ligands are exchanged for an enantiopure bidentate ligand.[12] Such an exchange reaction would require two prerequisites in terms of accessibility and reactivity of the new complexes: suitable reaction conditions for the ligand exchange reaction and similar, if not identical, coordinating properties of the new ligand and carbon monoxide.[13] In agreement with these prerequisites, we turned our attention toward bidentate phosphite ligands as described by Kündig.[14] These ligands have first been reported in 1988[14a] and have proven to be excellent CO-emulating ligands, thus resembling the electronic properties of CO itself. Extensive screening among all Kündig ligands revealed that ligand **2** (Scheme 1) gives the best results in thermal exchange reactions on the parent group 6 pentacarbonyl carbene complexes.[15] Thus, the complexation of ligand **2** with the molybdenum complex **1** is best carried out at 60 °C in toluene to furnish the desired complex **3** in 90% isolated chemical yield as the fac stereoisomer (Scheme 1).

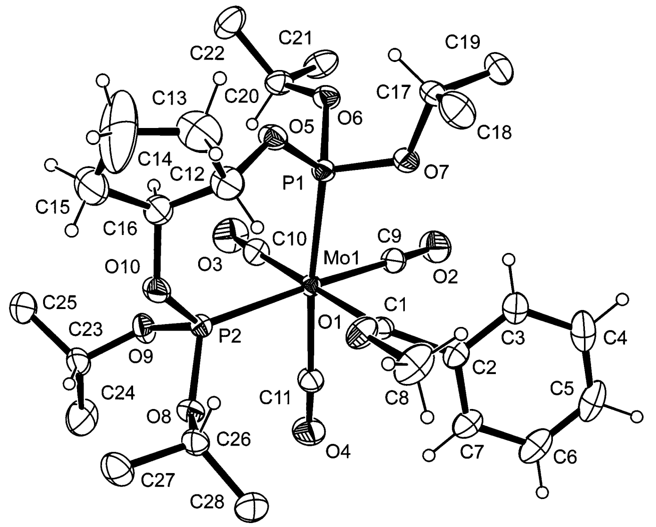


Figure 1. ORTEP diagram of *fac*-**3** drawn at the 25% probability level. Fluorine atoms are omitted for clarity.

While complex **3** is unstable in solution, it is fairly air-stable as an isolated solid.[16] Suitable crystals for X-ray analysis were grown from a diethyl ether solution. The solid-state structure of a racemic sample of *fac*-**3** is depicted in Figure 1. It should be noted that the two phosphorus atoms of the bidentate ligand occupy positions cis to the carbene moiety, resulting in an overall fac arrangement. This is in agreement with a kinetically favored dissociation of cis-ligated carbon monoxide ligands from **1**.

To the best of our knowledge, **3** is the first example of a successful replacement of two CO ligands for a chiral diphosphite ligand.[17] According to the known cis/trans isomerization of related monophosphine tetracarbonyl complexes,[11] the kinetic complex *fac*-**3** underwent conversion into the new complex *mer*-**3** when heated in an autoclave under an atmosphere of CO (20 bar, MeCN, 60 °C, 51%) (Scheme 2). The reaction could also be monitored by ^{31}P NMR when a solution of *fac*-**3** was submitted to temperature-dependent NMR spectroscopy. Thus, the two characteristic doublets of *fac*-**3** centered at 176.20 and 171.85 ppm gradually disappeared as the new set of signals of *mer*-**3** at 185.98 and 173.46 ppm developed; moreover, the coupling constant $^{3}J_{\mathrm{P-H}}$ decreased from 38 Hz for *fac*-**3** to 29 Hz for *mer*-

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[10] (a) Vorogushin, A. V.; Wulff, W. D.; Hansen, H.-J. *J. Am. Chem. Soc.* **2002**, *124*, 6512. (b) Hsung, R. P.; Wulff, W. D.; Challener, C. A. *Synthesis* **1996**, 773. (c) Dötz, K. H.; Tomuschat, P.; Nieger, M. *Chem. Ber./Recl.* **1997**, *130*, 1605. (d) Herrmann, R.; Ugi, I. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 788.

[11] Cooke, M. D.; Fischer, E. O. *J. Organomet. Chem.* **1973**, *56*, 279.

[12] For the replacement of two carbonyl ligands with 1,2-bis(diphenylphosphino)ethane on chromium Fischer carbene complexes, see: Arrieta, A.; Cossio, F. P.; Fernández, I.; Gómez-Gallego, M.; Lecea, B.; Mancheño, M. J.; Sierra, M. A. *J. Am. Chem. Soc.* **2000**, *122*, 11509.

[13] (a) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

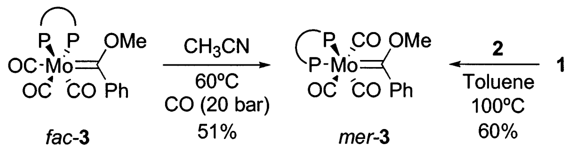
[14] (a) Cunningham, A. F., Jr.; Kündig, E. P. *J. Org. Chem.* **1988**, *53*, 1823. (b) Kündig, E. P.; Bourdin, B.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1856. (c) Kündig, E. P.; Saudan, C. M.; Bernadinelli, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1219. (d) Kündig, E. P.; Saudan, C. M.; Viton, F. *Adv. Synth. Catal.* **2001**, *343*, 51. (e) Kündig, E. P.; Saudan, C. M.; Alezra, V.; Viton, F.; Bernardinelli, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 4481.

[15] Muniz Fernandez, K. Diploma Thesis, Universidad de Oviedo/ Universität Hannover, 1996.

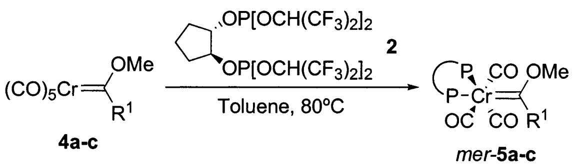
[16] This stability is noteworthy and has to be attributed to the introduction of the diphosphite ligand. The parent pentacarbonylmolybdenum complexes are known to be notoriously unstable; see: Harvey, D. F.; Brown, M. F. *Tetrahedron Lett.* **1990**, *31*, 2529.

[17] For the preparation of the achiral phosphinite complex *fac*-[Mo(CO)$_3${C(OMe)Me}{Ph$_2$POCH$_2$(CH$_2$OCH$_2$)$_2$CH$_2$OPPh$_2$}], as well as of related group 6 metal acylates, from M(CO)$_4${Ph$_2$POCH$_2$(CH$_2$OCH$_2$)$_2$CH$_2$OPPh$_2$}, see: Powell, J.; Gregg, M. R.; Kuksis, A.; May, C. J.; Smith, S. J. *Organometallics* **1989**, *8*, 2918.

Scheme 2



Scheme 3



entry	R^1	Yield (%)
a	Ph	80
b	Me	75
c	(*E*)-(CH=CH-2-furyl)	92

3.[18] The shift to lower field for the assumed trans-positioned phosphorus atom of *mer*-**3** relative to the signal for *fac*-**3** is a clear indication of the fac/mer isomerization. Alternatively, the straightforward formation of *mer*-**3** could be performed in 60% yield by prolonged heating to 100 °C in toluene of the pentacarbonyl carbene complex **1** with ligand **2** (Scheme 2).

There is no literature precedent for such an isomerization.[19] Although a dissociation−reassociation sequence cannot definitively be ruled out, this isomerization can be explained via an intermediate of trigonal-prismatic structure on the basis of the postulated isomerization of trans- and cis-configured monophosphine tetracarbonyl carbene complexes.[20]

Remarkably, the ligand exchange process with the corresponding chromium(0) complexes required heating at 80 °C and led directly to the thermodynamically stable mer isomer rather than to the fac isomer (Scheme 3). Thus, thermal exposure of simple pentacarbonyl(carbene)chromium complexes **4a**,**b** to ligand **2** in toluene resulted in the formation of *mer*-**5a**,**b** in good yields (75−80%). Significantly, the more useful and versatile chiral alkenylcarbene complexes are also available via carbonyl ligand exchange. For instance, carbene complex **4c** could be transformed into the chiral alkenyl carbene *mer*-**5c** (92% yield) under the same reaction conditions. Again, ^{31}P NMR data (δ 201 and 187 ppm; $^{3}J_{P-H} = 29-32$ Hz) were in complete agreement with a mer arrangement for complexes **5**. If any fac complex were involved, it should be only a short-lived, low-concentration intermediate escaping experimental identification.

The structure of complex **5b** was unambiguously determined by an X-ray analysis (Figure 2).

To summarize, we have described the synthesis, isolation, and characterization of novel tricarbonyl Fischer carbene complexes bearing enantiopure diphosphite ligands. This approach constitutes a very simple entry toward chiral nonracemic Fischer carbene complexes, which should find application in the area of asymmetric synthesis with group 6 metal carbenes. Actually, the use of these new complexes in asymmetric transformations, such as cyclopropanation[21] and benzannulation, among others, are being considered in our laboratory.

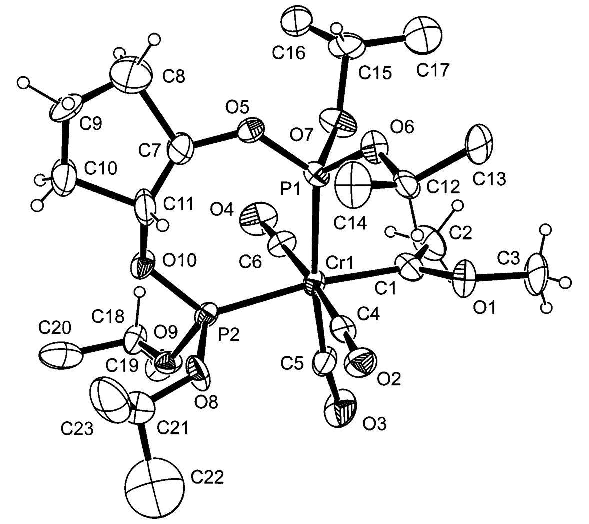


Figure 2. ORTEP diagram of *mer*-**5b** drawn at the 25% probability level. Fluorine atoms are omitted for clarity.

Experimental Section

Molybdenum hexacarbonyl and chromium hexacarbonyl were purchased. Toluene was distilled from sodium−benzophenone ketyl under nitrogen. All other reagents and solvents were reagent grade, were distilled prior to use, and were stored under a nitrogen atmosphere. The parent pentacarbonyl complexes of molybdenum **1**[16] and chromium **4**[22] and the chiral ligand **2**[14a] were synthesized according to literature methods. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator. Flash column chromatography was carried out on silica gel 60 (230−240 mesh). IR spectra were obtained in a Mattson 3000 FTIR spectrometer. ^{1}H NMR (200, 300 MHz) and ^{13}C NMR (50.5, 75.5 MHz) spectra were measured at room temperature on Bruker AC-200 and AC-300 instruments, respectively, with tetramethylsilane as internal standard. Mass spectra were determined on a Finnigan MAT 95 spectrometer. Elemental analyses were carried out on Perkin-Elmer 2400 and Carlo Erba 1108 microanalyzers.

***fac*-{*trans*-1,2-Bis[bis(2,2,2-trifluoro-1-(trifluoromethyl)ethoxy)phosphinoxy]cyclopentane}tricarbonyl(methoxyphenylmethylene)molybdenum(0) (*fac*-3).** Under an inert-gas atmosphere, a well-dried Schlenk flask was charged with 0.26 g (0.73 mmol) of pentacarbonyl(methoxyphenylmethylene)molybdenum(0) (**1**). Freshly distilled toluene (30 mL) and 0.61 g (0.73 mmol) of ligand **2** were added, and the resulting solution was heated at 60 °C for 3 h (IR monitoring). Toluene was removed under reduced pressure, and the remaining red oily residue was chromatographed (SiO_2, 10/1 v/v hexane/ethyl acetate) under a nitrogen atmosphere to give *fac*-**3** (0.74 g, 90% yield) as a bright red solid.

IR (THF): ν 2002 (s), 1946 (m), 1911 (m) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.6−1.85 (m, 4H), 2.2 (m, 2H), 3.85 (s, 3H), 4.70 (m, 1H), 4.9−5.2 (m, 3H), 5.3 (m, 2H), 6.8 (m, 2H),

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[18] See the Supporting Information for reproduction of ^{31}P NMR and IR spectra.

[19] (a) Such an isomerization has been described for certain tungsten carbene complexes bearing bis-phosphine ligands. However, these complexes do not represent the classical electronic structures of Fischer carbene complexes; see: Schenk, W. A.; Kümmerle, D.; Burschka, C. *J. Organomet. Chem.* **1988**, *349*, 183. (b) Heating *fac*-**3** in the absence of carbon monoxide resulted in slow decomposition.

[20] Fischer, H.; Fischer, E. O.; Werner, H. *J. Organomet. Chem.* **1974**, *73*, 331.

[21] Barluenga, J.; Muñiz, K.; Ballesteros, A.; Martínez, S.; Tomás, M. *ARKIVOC* **2002**, *3* (Part V), 110.

[22] Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445.

7.3 (m, 1H), 7.45 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 23.1 (s, CH_2), 34.0 (t, $J_{C-P} = 8.3$ Hz, $2CH_2$), 65.7 (s, OCH_3), 68.8−72.0 (m, 4CH), 86.0 (d, $J_{C-P} = 129.2$ Hz, 2CH), 118.8 (s, $2CH_{arom}$), 121.4, (q, $J_{C-F} = 293.6$ Hz, $8CF_3$), 129.1 (s, CH_{arom}), 129.3 (s, $2CH_{arom}$), 152.3 (s, C_{arom}), 210.4−211.7 (m, 2CO), 221.9 (br s, CO), 349.3 (t, $J_{C-P} = 14.5$ Hz, C═Mo). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 171.7 (d, $J_{P-P} = 38$ Hz), 176.2 (d, $J_{P-P} = 39.2$ Hz). Anal. Found for $C_{28}H_{20}F_{24}MoO_{10}P_2$: C, 29.66; H, 1.37. Calcd: C, 29.75; H, 1.78. FAB-MS (^{98}Mo): *m/z* 1132 (M^+, 10%), 1048 ($M^+ - 3CO$, 100%).

(−)-*fac*-{*trans*-1,2-Bis[bis(2,2,2-trifluoro-1-(trifluoromethyl)ethoxy)phosphinoxy]cyclopentane}tricarbonyl(methoxyphenylmethylene)molybdenum(0) (*fac*-3). $[\alpha]^{25}_{D} = -67.02°$ ($c = 1.5$, $CHCl_3$).

***mer*-{*trans*-1,2-Bis[bis(2,2,2-trifluoro-1-(trifluoromethyl)ethoxy)phosphinoxy]cyclopentane}tricarbonyl(methoxyphenylmethylene)molybdenum(0) (*mer*-3). (a) By Isomerization of *fac*-3.** Complex *fac*-**3** (0.45 g, 0.4 mmol) was dissolved in 20 mL of freshly distilled acetonitrile in an autoclave. The autoclave was charged with carbon monoxide (20 bar) and heated at 60 °C for 3 h. The autoclave was then purged with a positive stream of nitrogen, the solution was transferred into a Schlenk flask, and the solvent was removed under reduced pressure. The remaining slightly greenish yellow oil was crystallized from dichloromethane to yield *mer*-**3** (0.23 g, 51% yield) as a bright orange solid.

(b) From the Pentacarbonyl Complex 1 and Ligand 2. Under an inert-gas atmosphere, a well-dried Schlenk flask was charged with 0.43 g (1.3 mmol) of pentacarbonyl(methoxyphenylmethylene)molybdenum(0) (**1**) and 1.08 g (1.3 mmol) of ligand **2**. Freshly distilled toluene (30 mL) was added, and the resulting solution was heated at 100 °C for 3 h (IR monitoring). Toluene was removed under reduced pressure, and the remaining red oily residue was chromatographed (SiO_2, 10/1 v/v hexane/ethyl acetate) under a nitrogen atmosphere to give a residue which was crystallized from dichloromethane. After fractional crystallization the complex *mer*-**3** (0.88 g, 60% yield) was obtained as a bright orange solid.

IR (CH_3CN): 2021 (w), 1954 (m), 1921 (s) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.6−1.8 (m, 4H), 2.1−2.2 (m, 2H), 4.2 (s, 3H), 4.6 (m, 2H), 4.9−5.4 (m, 4H), 7.1 (m, 2H), 7.3−7.6 (m, 3H). ^{31}P NMR (121 MHz, CH_3CN): δ 170.1 (d, $J_{P-P} = 32.6$ Hz), 185.7 (d, $J_{P-P} = 39.5$ Hz). Anal. Found for $C_{28}H_{20}F_{24}MoO_{10}P_2$: C, 29.59; H, 1.39. Calcd: C, 29.75; H, 1.78.

General Procedure for the Preparation of Chromium Complexes 5. Under an inert-gas atmosphere, a well-dried Schlenk flask was charged with the corresponding chromium carbene complex **4** (0.38 mmol). Freshly distilled toluene (30 mL) and ligand **2** (0.32 g, 0.38 mmol) were added, and the resulting solution was heated at 80 °C for 5 h (IR monitoring). Toluene was removed under reduced pressure, and the remaining oily residue was chromatographed (SiO_2, 10/1 v/v hexane/ethyl acetate) under a nitrogen atmosphere to give complexes *mer*-**5a** (0.33 g, 80% yield; orange solid), *mer*-**5b** (0.29 g, 75%; yellow solid), and *mer*-**5c** (0.38 g, 92%; red solid).

***mer*-{*trans*-1,2-Bis[bis(2,2,2-trifluoro-1-(trifluoromethyl)ethoxy)phosphinoxy]cyclopentane}tricarbonyl(methoxyphenylmethylene)chromium(0) (*mer*-5a).** IR (hexane): ν 1982 (w), 1961 (m), 1919 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.6−1.8 (m, 4H), 2.2 (m, 2H), 3.95 (s, 3H), 4.6 (m, 2H), 4.9 (m, 1H), 5.1 (m, 1H), 5.2 (m, 1H), 5.4 (m, 1H), 7.0 (m, 2H), 7.3 (m, 1H), 7.4 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 21.0 (s, CH_2), 32.3 (t, $J_{C-P} = 7.6$ Hz, $2CH_2$), 64.8 (s, OCH_3), 69.1−70.9 (m, 4CH), 83.7 (d, $J_{C-P} = 60.8$ Hz, 2CH), 119.7 (s, $2CH_{arom}$), 120.6 (q, $J_{C-F} = 282.2$ Hz, $8CF_3$), 128.2 (s, $2CH_{arom}$), 128.6 (s, CH_{arom}), 151.5 (d, $J_{C-P} = 4.4$ Hz, C_{arom}), 217.6 (dd, $J_{C-P} = 20.7$, 17.4 Hz, CO), 218.7 (dd, $J_{C-P} = 22.3$, 15.8 Hz, CO), 220.5 (d, $J_{C-P} = 22.9$ Hz, CO), 352.2 (dd, $J_{C-P} = 25.1$, 5.5 Hz, C═Cr). ^{31}P NMR (81 MHz, $CDCl_3$): δ 187.1 (d, $J_{P-P} = 34.4$ Hz), 200.8 (d, $J_{P-P} = 32.2$ Hz). Anal. Found for $C_{28}H_{20}CrF_{24}O_{10}P_2$: C, 30.78; H, 1.55. Calcd: C, 30.96; H, 1.86. FAB-MS: *m/z* 1086 (M^+, 11%), 1002 ($M^+ - 3CO$, 100%).

***mer*-{*trans*-1,2-Bis[bis(2,2,2-trifluoro-1-(trifluoromethyl)ethoxy)phosphinoxy]cyclopentane}tricarbonyl(methoxymethylmethylene)chromium(0) (*mer*-5b).** IR (hexane): ν 2013 (w), 1961 (m), 1902 (s) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.6−1.8 (m, 4H), 2.2 (m, 2H), 3.0 (s, 3H), 4.25 (s, 3H), 4.65 (m, 2H), 5.0 (m, 2H), 5.2 (m, 2H). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 21.9 (s, CH_2), 33.3 (d, $J_{C-P} = 6.6$ Hz, $2CH_2$), 53.9 (s, CH_3), 63.6 (s, OCH_3), 69.6−71.6 (m, 4CH), 84.6 (d, $J_{C-P} = 56.1$ Hz, 2CH), 121.4 (q, $J_{C-F} = 283.2$ Hz, $8CF_3$), 219.0−220.1 (m, 2CO), 222.2 (d, $J_{C-P} = 29.5$ Hz, CO), 359.1 (dd, $J_{C-P} = 28.1$, 6.1 Hz, C═Cr). ^{31}P NMR (81 MHz, $CDCl_3$): δ 187.0 (d, $J_{P-P} = 29.9$ Hz), 200.0 (d, $J_{P-P} = 29.2$ Hz). Anal. Found for $C_{23}H_{18}CrF_{24}O_{10}P_2$: C, 26.93; H, 1.41. Calcd: C, 26.97; H, 1.77. FAB-MS: *m/z* 1025 ($M^+ + 1$, 11%), 940 ($M^+ - 3CO$, 100%).

***mer*-{*trans*-1,2-Bis[bis(2,2,2-trifluoro-1-(trifluoromethyl)ethoxy)phosphinoxy]cyclopentane}tricarbonyl{methoxy[2-(2-furyl)ethenyl]methylene}chromium(0) (*mer*-5c).** IR (THF): ν 2004 (w), 1950 (s), 1896 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.6−1.8 (m, 4H), 2.2 (m, 2H), 4.5 (s, 3H), 4.7 (m, 2H), 4.9 (m, 1H), 5.0 (m, 1H), 5.15 (m, 2H), 6.5 (m, 1H), 6.75 (m, 1H), 6.9 (d, $J = 13.5$ Hz, 1H), 7.55 (m, 1H), 7.7 (d, $J = 13.5$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.0 (s, CH_2), 32.5 (t, $J_{C-P} = 6.6$ Hz, $2CH_2$), 64.1 (s, OCH_3), 69.1−71.2 (m, 4CH), 83.6 (d, $J_{C-P} = 43.0$ Hz, 2CH), 112.9 (s, CH_{furyl}), 117.8 (s, CH_{furyl}), 120.5, (q, $J_{C-F} = 279.8$ Hz, $8CF_3$), 121.7 (s, CH), 135.6 (d, $J_{C-P} = 5.4$ Hz, CH), 145.6 (s, CH_{furyl}), 151.3 (s, C_{furyl}), 219.2 (t, $J_{C-P} = 21.3$ Hz, CO), 220.8 (t, $J_{C-P} = 20.6$ Hz, CO), 221.1 (t, $J_{C-P} = 16.9$ Hz, CO), 320.7 (m, C═Cr). ^{31}P NMR (121 MHz, $CDCl_3$): δ 187.4 (d, $J_{P-P} = 28.7$ Hz), 198.1 (d, $J_{P-P} = 28.7$ Hz). Anal. Found for $C_{28}H_{20}CrF_{24}O_{11}P_2$: C, 30.33; H, 1.59. Calcd: C, 30.51; H, 1.83.

X-ray Structure Determinations. General Considerations. The most relevant crystal and refinement data are collected in Table 1. Diffraction data were recorded on a Nonius CAD4 single-crystal diffractometer. The intensities were measured using the $\omega-2\theta$ scan technique with a scan angle of 1.5° intensity of the primary and a variable scan rate with a maximum scan time of 60 s per reflection. The beam was checked throughout the collection by monitoring three standard reflections every 60 min. On all reflections, profile analysis was performed.[23] Some double-measured reflections were averaged, and Lorentz and polarization corrections were applied. The space groups were inferred from systematic absences. The structures were solved by Patterson interpretation and phase expansion using DIRDIF.[24] Isotropic least-squares refinement on F^2 was carried out using SHELXL93.[25] Absorption correction was applied to *fac*-**3** by means of XABS2.[26] During the final stages of the refinements, all positional parameters and the anisotropic temperature factors of all the non-H atoms were refined. The H atoms were geometrically located and refined riding with common isotropic thermal parameters. Four highly disordered CF_3 terminal groups were refined using two alternative positions for the F atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$ and the coefficients of P^2 and P are 0.1247 and 5.6410 for *mer*-**5b** and 0.0721 and 1.5632 for *fac*-**3**, respectively, with $\sigma(F_o^2)$ from counting statistics and

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(23) (a) Lehman, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A* **1974**, *30*, 580. (b) Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1978**, *11*, 114.

(24) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF Program System; Technical Report of the Crystallographic Laboratory; University of Nijimegen, Nijimegen, The Netherlands, 1992.

(25) Sheldrick, G. M. SHELXL-93. In *Crystallographic Computing 6*; Flack, H. D., Parkanyi, P., Simon, K., Eds.; IUCr/Oxford University Press: Oxford, U.K., 1993.

(26) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.

Table 1. Crystallographic Data for *fac*-3 and *mer*-5b

	fac-**3**	*mer*-**5b**
empirical formula	$C_{28}H_{20}F_{24}MoO_{10}P_2$	$C_{23}H_{18}CrF_{24}O_{10}P_2$
fw	1130.32	1024.31
temp (K)	293(2)	293(2)
wavelength (Å)	0.717 03	0.710 73
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
a (Å)	10.937(5)	10.080(16)
b (Å)	20.892(17)	15.74(3)
c (Å)	17.882(8)	23.566(6)
β (deg)	93.28(7)	
V (Å^3)	4079.0(42)	3739(10)
Z; calcd density (Mg/m^3)	4; 1.841	4; 1.820
abs coeff (mm^{-1})	0.560	0.560
F(000)	2224	2024
crystal size (mm)	0.5 × 0.43 × 0.36	0.21 × 0.19 × 0.07
θ range for data collecn (deg)	1.50−24.99	1.56−26.00
limiting indices	$0 \le h \le 12$, $0 \le k \le 24$, $-21 \le l \le 21$	$0 \le h \le 12$, $0 \le k \le 19$, $0 \le l \le 29$
no. of rflns collected/ unique	7781/7162 (R(int) = 0.017)	4107/4107
abs cor	empirical	none
max and min transmissn	1.025 and 0.937	
refinement method	full-matrix least squares on F^2	
no. of data/restraints/ params	7162/0/587	4107/24/509
goodness of fit on F^2	1.105	0.999
final R indices ($I > 2\sigma(I)$)	R1 = 0.0408, wR2 = 0.1172	R1 = 0.0714, wR2 = 0.1822
R indices (all data)	R1 = 0.0628, wR2 = 0.1206	R1 = 0.2956, wR2 = 0.2799
largest diff peak and hole (e/Å^3)	0.624 and −0.408	0.508 and −0.465

$P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$. Atomic scattering factors were taken from ref 27. Plots were made with the EUCLID package.[28] Geometrical calculations were made with PARST.[29] All calculations were carried out at the Scientific Computer Centre of the University of Oviedo on the X-ray group computers.

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Supporting Information Available: Tables giving X-ray crystallographic data for compounds *fac*-**3** and *mer*-**5b**. Figures giving ^{31}P NMR spectra for the *fac*-**3** to *mer*-**3** isomerization. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0210560

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(27) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV. (present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands).

(28) Spek, A. L. PLATON, a Multipurpose Crystallographic Tool; Utrecht University, Utrecht, The Netherlands, 2000.

(29) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.