37. New C_2-Chiral Bidentate Ligands Bridging the Gap between Donor Phosphine and Acceptor Carbonyl Ligands

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(27.XII.93)

Two new C_2 chiral bidentate phosphorous ligands have been prepared in enantiomerically pure form. The two phosphorous centers bear electron-withdrawing groups ($(CF_3)_2CH–O$, C_6F_5) and are linked by a *trans*-cyclopentane-1,2-diol-derived bridge. Photolysis of $[Cr(\eta^6-C_6H_6)(CO)_3]$ in the presence of these two new ligands and of two previously reported bidentate phosphites, and fluorophosphinites (L) afforded $[Cr(\eta^6-C_6H_6)(CO)L]$ complexes. IR Spectral comparison of the complexes shows the new ligands to be intermediate in their bonding properties between alkyl phosphites and CO.

Introduction. – Chiral phosphorous ligands play a central role in homogeneous asymmetric catalysis (for a review, see [1]). A very large number of chiral electron-rich phosphine ligands have been reported, and many are now commercially available [2]. Chelating ligands are often the most efficient, both in terms of catalytic activity and stereoselectivity. Compared to monodentate ligands, their interaction with a metal center favors catalytic activity in asymmetric transformations through a higher resistance to metal–ligand bond cleavage and through conformational restraint.

For a long time, much of the incentive in synthesizing new chiral ligands came from the asymmetric hydrogenation of prochiral olefins, the first highly successful example being the reduction of (*Z*)-α-acetamidocinnamic acid [3]. Chiral Rh-diphosphine complexes are efficient catalysts for this asymmetric reaction. Thereafter, this became the test reaction for new chiral phosphine ligands [1][2].

Less electron-rich bidentate phosphorous ligands have seen slower development. Bidentate π-acceptor fluorophosphines $F_2P(C_6H_{10})PF_2$, $F_2PCX_2CX_2PF_2$ ($X = H,F$), and $RN(PF_2)_2$ have been known for some time [4]. Recently, convenient syntheses of bidentate fluoroalkylphosphines – notably $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ [5] and $(CF_3)_2PCF_2CF_2P(CF_3)_2$ [6] – have been reported and coordinated to transition metals [5–7]. To our knowledge, these ligands, which emulate the bonding characteristics of carbon monoxide have not yet found application in catalysis.

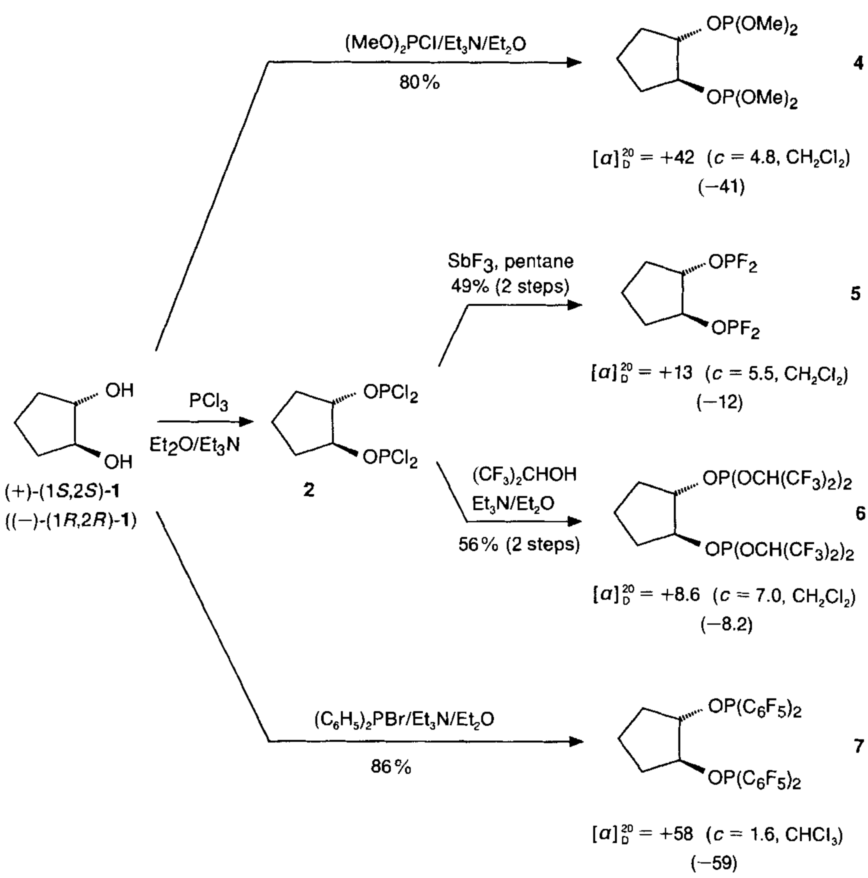
Carbon monoxide is an ubiquitous ligand in organometallic chemistry [8]. Its ability to stabilize transition-metal centers in low oxidation states is associated with its π-acidic properties. Metal-carbonyl complexes are widely used starting materials in organometallic reactions and metal-carbonyl complex fragments play an important role in the stoichiometric and catalytic transformation of organic molecules [8] [9]. The replacement of two *cis*-CO ligands by a chiral ligand with a similar bonding characteristic may lead to new asymmetric catalysts. Reports on chiral non-racemic π-acidic ligands are scarce (for a first example, see [10]). We believe that this will change rapidly, because it has become evident from a number of reports in recent years that certain transition-metal-catalyzed transformations are more successful when less electron-rich ligands are used. These include Ni^0-catalyzed diene cyclodimerizations [11], and Rh^I-catalyzed alkene hydroformylation [12] and [4 + 2] cycloaddition reactions [13]. In all three transformations, the good π-acceptor ligand $P(OCH(CF_3)_2)_3$ is particularly efficient. A bidentate phosphite ligand was essential in Pd-catalyzed trimethylenemethane cycloadditions [14], and yet another chelating phosphite ligand gave high *n*/iso ratios of aldehydes in Rh-catalyzed hydroformylation of terminal olefins [15] with excellent compatibility with a wide number of functional groups [16]. Applications in asymmetric catalysis are as yet rare. One recent example involves a binary Ni complex of an enantiomerically pure aryl diphosphite ligand, derived from (*R*)-2,2′-binaphthol. It catalyzes the hydrocyanation of norbornene with an ee of 38% [17]. More dramatically, *Nugent et al.* found that, on introducing electron-withdrawing groups in a bidentate aryl diphenylphosphinite ligand with a sugar backbone, enantiomeric excess increased from 40 to 91% in the same reaction [18]. These examples and the numerous reactions catalyzed or mediated by transition-metal-carbonyl complexes, make the development of chiral bidentate ligands with electronic properties intermediate between the electron-rich phosphines and the π-acceptor CO timely and desirable for new applications in asymmetric catalysis.

For the backbone of our ligands we chose *trans*-cyclopentane-1,2-diol (**1**) [19]. The cyclopentane unit provides the desired rigidity and the *trans*-configuration ensures that undesirable intramolecular cyclization to a single P center cannot take place. Previous reports on the synthesis and use in asymmetric catalysis of bidentate ligands based on *trans*-substituted cyclopentane include *trans*-1,2-bis(diphenylphosphinoxy)cyclopentane [20] and *trans*-1,2-bis(diphenylphosphino)cyclopentane [21]. Enantiomerically enriched ligands were obtained by partial (67%) resolution of the diol in the former case; by resolution of the racemic ligand *via* formation of a diastereoisomeric Ni complex in the latter case. Both ligands are efficient in asymmetric homogenous hydrogenation catalysis using Rh complexes.

Nowadays, both enantiomers of *trans*-cyclopentane-1,2-diol (**1**) are accessible by synthesis from diethyl tartrate [10] or by enzyme-catalyzed ester hydrolysis [22] or acetate transfer [23]. In earlier work, we described the transformation of **1** into the enantiomerically pure C_2 chiral bidentate phosphite (**4**) and fluorophosphinite (**5**) ligands [10]. Here, we report the synthesis of the two new chiral bidentate ligands **6** and **7** and the evaluation of the donor/acceptor properties of the ligands **4**–**7** in the complexes [Cr(η^6-benzene)(CO)(L)] (**9**–**12**).

Results and Discussion. – 1. *Synthesis of Ligands* **6** *and* **7**. The new chiral bidentate ligands **6** and **7** were prepared *via* methodology previously used for **4** and **5** [10] (*Scheme 1*). For the hexafluoroisopropoxy phosphite **6**, an etheral solution of racemic diol **1** and NEt_3 was added to an excess of PCl_3 in Et_2O at 0° [24] [25]. The crude 1,2-bis(dichlorophosphinoxy)cyclopentane (**2**), obtained as a yellow oil, was reacted with $(CF_3)_2CHOH$ and NEt_3 to give, after vacuum distillation, **6** as a colorless oil in 56% yield (based on **1**). A reversed sequence of reactions was found advantageous for ligand **7**. Following the procedure in [26], the C_6F_5 groups were introduced *via* addition of the *Grignard* reagent PhMgBr to a solution of 0.5 equiv. of PCl_3 in Et_2O at 0°. Fractional distillation under vacuum yielded, as described in [26a], the halide-exchanged bromo product $(C_6F_5)_2PBr$ (**3**) as a yellow oil in 60% yield. Its reaction with **1** afforded crystalline **7** in 86% yield. The optically active ligands (+)-(1*S*,2*S*)- and (–)-(1*R*,2*R*)-**6** and -**7** were analogously prepared using the appropriate cyclopentanediol enantiomer.

Scheme 1

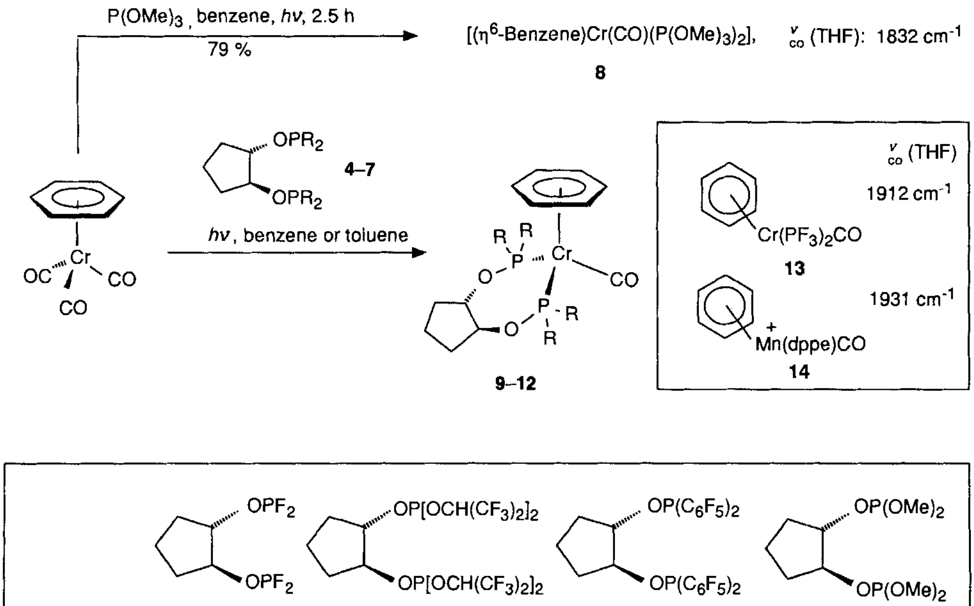


The electronic nature of phosphorous ligands can be expressed in terms of the electronic parameter χ. Introduced by *Tolman* [27], χ is derived from the A_1 IR frequency of the ν(CO) mode in the complex $[Ni(CO)_3(PR_3)]$. The χ values lie in the range of 0–12 for alkyl and aryl phosphines, 18–33 for phosphites, and 33–51 for fluoroalkyl phosphites (*e.g.* 51.3 for the previously mentioned $P(OCH(CF_3)_2)_3)$ [11]. Even higher values are found for the strong acceptor ligands PF_3 (χ = 54.6) and $P(CF_3)_3$ (χ = 58.8). The χ values for **4**–**7** were determined using the procedure in [27a] and found to increase in the order **4** (χ = 23.3) < **7** (31.1) < **5** (42.2) < **6** (43.5). In a good approximation, R groups in $PR^1R^2R^3$ contribute additively to χ. Applied to **4**–**7**, the high χ value of 45.3 would be expected for **5**. Deviation from additivity has been observed before in mixed ligands and found to be linked to the donor/acceptor properties of the atoms in the α-position of phosphorus [28].

2. *Synthesis of the Complexes [Cr(η^6-C_6H_6)(CO)L]* (**9**–**12**). To test further our hypothesis that the new ligands emulate some of the bonding characteristics of CO, we prepared the [Cr(benzene)(CO)L] complexes. The synthesis itself provided a first part of the answer. It is well established that photolysis of [Cr(benzene)$(CO)_3$] results in the stepwise substitution of one or several CO groups [29]. With electron-rich phosphines (PR_3, PPh_3), the reaction stops at the [Cr(benzene)$(CO)_2$L] stage, because the increased electron density at the metal results in stronger binding of the remaining CO ligands [30]. The less basic phosphite ligands lead to mixtures of complexes [Cr(benzene)$(CO)_n(P(OR)_3)_{3-n}$] (n = 0–2) [31]. We found that, with a large excess of $P(OMe)_3$, the exchange can be driven completely to [Cr(benzene)(CO)$(P(OMe)_3)_2$] (**8**; see *Exper. Part*). Finally, all three CO ligands can be exchanged with PF_3, a ligand which has similar bonding properties to carbon monoxide[1]). Although entropy makes the second CO substitution more favorable with bidentate ligands, its success depends largely on the *Lewis* acid/base properties of the ligands coordinated to the metal.

The reaction proceeded readily with all four ligands **4**–**7**. Irradiation of a benzene or toluene solution of [Cr(benzene)$(CO)_3$] and an equimolar amount of the appropriate ligand (*Scheme 2*) afforded the complexes **9**–**12**. The reaction was monitored by the disappearance of the ν(CO) bands of the starting complex and the mono-substituted

Scheme 2



ligand :	**5** (χ = 42.2)	**6** (43.5)	**7** (31.1)	**4** (23.3)
complex, (yield %):	**10** (45)	**11** (84)	**12** (86)	**9** (68)
ν_{co} (THF):	1874 cm^{-1}	1865 cm^{-1}	1868 cm^{-1}	1829 cm^{-1}

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[1]) For an overview of PF_3 complexes of transition metals, see [32a].

intermediate and continued until a single band was present. The IR ν(CO) band is a quantatitive probe of the electronic properties of the ligands **4**–**7**. Its position is very sensitive to changes in electron density at the metal and reflects π-backbonding into the CO π^* orbital. The values obtained for the complexes **9**–**12** are shown in *Scheme 2* together with those of the benzene complexes containing the fragments $[Cr(CO)(PF_3)_2]$ (**13**) [32b], and $[Mn(CO)(dppe)]^+$ (**14**) [33], both included here because of their close electronic resemblance to the $Cr(CO)_3$ group. In accord with our expectation, the ν(CO) values of the complexes **10**–**12** containing the three more electron-withdrawing ligands **5**–**7** are intermediate between those of the phosphite complex **9** and the strongly electrophilic complexes **13** and **14**. The values do not, however, follow the pattern set by χ. Notably, complex **12**, containing ligand **7**, has a ν(CO) band some 15 cm^{-1} higher than expected. While the present data do not allow detailed interpretation, we have to keep in mind that χ was determined in a complex where the ligands are coordinated *via* a single P center, whereas in **9**–**12** they function as bidentate ligands. Also, the changes brought about by the more congested coordination sphere affect the ligand binding and, thus, the position of the ν(CO) band.

In conclusion, we have shown that the two new bidentate ligands of C_2 chirality can be efficiently prepared. In their electronic characteristics, the ligands of this series bridge the gap between phosphites and the π-acidic CO. This opens new prospects for metal-mediated reactions by transition-metal fragments in which two *cis*-CO groups are replaced by a chiral bidentate ligand which emulates bonding characteristics of CO. Electronic factors apart, asymmetric induction will depend on the ligand's ability to provide a chiral environment close to the reaction center. We, therefore, may speculate on the relative applicability of the ligands **5**–**7** in asymmetric reactions. In bidentate ligands of C_2 symmetry and containing chiral centers in the ligand backbone, asymmetric induction is transmitted *via* the spatial arrangement imposed on the two residual groups at the P centre [2]. While the size and electronic properties of the bis(difluorophosphinoxy) ligand **5** come closest to PF_3 and CO, the small F groups are unlikely to be efficient in transmitting chiral information. The hexafluoroisopropyl ligand **6** and the pentafluorophenyl ligand **7** are more promising candidates. Their application in asymmetric catalysis is presently under study in our laboratory.

We are grateful for financial support of this work by the *Swiss National Science Foundation*. We also wish to thank Mr. *J. P. Saulnier*, Mr. *A. Pinto*, and Mrs. *D. Clément* for NMR and MS measurements.

Experimental Part

1. *General*. All reactions were carried out under an atmosphere of purified N_2 and with an inert gas/vacuum double manifold and standard *Schlenk* techniques. $Cr(CO)_6$ was obtained from *Pressure Chemicals* or *Strem Chemicals* and used as received in the synthesis of $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ [34]. THF, Et_2O were distilled from sodium-benzophenone ketyl immediately prior to use. Hexane, benzene, and Et_3N were distilled from CaH_2. Toluene was refluxed over Na before distillation. Bromopentafluorobenzene (*Aldrich*) was used as received. PCl_3 (*Fluka*) and $(CF_3)_2CHOH$ (*Fluka*) were distilled. *trans*-Cyclopentane-1,2-diol was prepared as described in [35]. M.p. were determined on a *Büchi 510* apparatus and are not corrected. Optical rotations were measured on a *Perkin-Elmer-241* polarimeter. Anal. TLC were carried out by using *Merck* silica-gel *60 F_{254}* plates. IR Spectra were recorded on a *Mattson-Instruments Polaris* FT spectrometer and a *Perkin Elmer 1600 Series* FTIR spectrometer by using NaCl soln. cells. ^1H-, ^{19}F-, ^{31}P-, and ^{13}C-NMR Spectra were recorded on a *Varian-XL-200* or a *Bruker-AMX400* spectrometer. Chemical shifts (δ) are given in ppm relative to TMS, C_6F_6, and H_3PO_4, respectively, and

coupling constants (J) in Hz. EI-MS (70 eV) were obtained on a *Varian CH 4* or *SM 1* spectrometer; relative intensities are given in parentheses. Elemental analyses were performed by *H. Eder*, Service de Microchimie, Institut de Chimie Pharmaceutique, Université de Genève.

2. *Ligands.* trans-*1,2-Bis{bis[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]phosphinoxy}cycylopentane* (**6**). To a stirred soln. of PCl_3 (12 ml, 0.138 mol) in Et_2O (80 ml) at 0° was added dropwise a soln. of *trans*-cyclopentane-1,2-diol (**1**, 0.716 g, 7 mmol) in Et_2O/Et_3N 7.5:1 (17 ml). A white precipitate formed immediately. After stirring for 1 h at the same temp., the mixture was filtered through *Celite*, and stripped of volatiles under vacuum. The resulting yellow oil (trans-*1,2-bis(dichlorophosphinoxy)cyclopentane* (**2**)) was dissolved in Et_2O (100 ml) and treated at 0° with a soln. of 2,2,2-trifluoro-1-(trifluoromethyl)ethanol (3 ml, 29 mmol) in 3.5:1 Et_2O/Et_3N (20 ml). After stirring overnight at 20°, the mixture was filtered over *Celite*. Concentration yielded a pale yellow oil. Distillation at $2 \cdot 10^{-5}$ mbar, 49–51° gave **6** (3.273 g, 56%) as colorless oil. IR (CH_2Cl_2): 1375*s*, 1294*s*, 1268*s*, 1228v*s*, 1202v*s*, 1109*s*, 991*s*, 900*s*, 873*s*, 796*m*. ^1H-NMR (200 MHz, $CDCl_3$): 4.60–4.90 (*m*, 6 H); 1.90–2.20 (*m*, 2 H); 1.70–1.90 (*m*, 4 H). ^{19}F-NMR (188 MHz, $CDCl_3$): 87.2–87.6 (*m*). ^{31}P-NMR (81 MHz, $CDCl_3$): 141.4–142.3 (*m*). MS: 679 (25), 464 (40), 449 (30), 399 (40), 382 (20), 365 (30), 151 (25), 129 (40), 83 (15), 67 (100). Anal. calc. for $C_{17}H_{12}F_{24}O_6P_2$: C 24.59, H 1.46; found: C 24.63, H 1.43.

The ligands (+)-(1*S*,2*S*)-**6** and (–)-(1*R*,2*R*)-**6** were obtained by the same procedure using enantiomerically pure cyclopentanediol. (+)-(1*S*,2*S*)-**6**: $[\alpha]_D^{20} = +8.6$ ($c = 7.0$, CH_2Cl_2). (–)-(1*R*,2*R*)-**6**: $[\alpha]_D^{20} = -8.2$ ($c = 7.0$, CH_2Cl_2).

Bis(pentafluorophenyl)bromophosphine (**3**) [26]. A soln. of C_6F_5Br (12.5 ml, 0.100 mol) in Et_2O (30 ml) was added dropwise to a refluxing suspension of Mg turnings (2.964 g, 0.122 mol), activated previously by a few grains of I_2 in Et_2O (30 ml)[2]). The mixture was stirred overnight at 20°, filtered over *Celite*, concentrated and then distilled under vacuum (10^{-2} mbar, 62–66°) to give **3** as pale yellow oil (13.29 g, 60%). ^{19}F-NMR (188 MHz, $CDCl_3$): 33.34–33.64 (*m*, 4 F); 15.02–15.04 (*m*, 2 F); 2.02–2.22 (*m*, 4 F). ^{31}P-NMR (81 MHz, $CDCl_3$): 11.8 (*quint.*, $J = 35.5$). MS: 446 (2), 444 (2), 365 (10), 296 (9), 217 (14), 129 (28), 117 (30), 110 (15), 98 (12), 93 (16), 79 (13), 69 (100), 47 (9).

trans-*1,2-Bis[bis(pentafluorophenyl)phosphinoxy]cyclopentane* (**7**). To a stirred soln. of **1** (2.686 g, 26 mmol) and Et_3N (7.3 ml, 52 mmol) in Et_2O (300 ml) at 0° was added dropwise $(C_6F_5)_2PBr$ (**3**, 23.283 g, 52 mmol). A white precipitate appeared immediately. The mixture was stirred at 20° overnight, filtered, and taken to dryness under reduced pressure. Polymeric materials were removed by filtration on SiO_2 in CH_2Cl_2. The crude solid off-white product was taken up in hot hexane and recrystallized at 0° to give colorless crystals of **7** (18.640 g, 86%). M.p. 92–94°. ^1H-NMR (200 MHz, $CDCl_3$): 4.30–4.50 (*m*, 2 H); 1.90–2.15 (*m*, 2 H); 1.65–1.90 (*m*, 4 H). ^{13}C-NMR (50 MHz, CD_2Cl_2): 20.6 (CH_2); 30.8 (*d*, $J = 7$, CH_2); 88.4 (*dd*, $J = 7, 25$, CHO); 135–150 (*m*, arom. C). ^{31}P-NMR (81 MHz, $CDCl_3$): 87.95 (*quint.*, $J = 34.3$). IR (CH_2Cl_2): 2956*w* (br.), 1640*m*, 1517*s*, 1476v*s*, 1381*m*, 1290*m*, 1090*s*, 981*s*. MS: 747 (16), 448 (15), 383 (22), 382 (22), 365 (48), 296 (17), 215 (17), 67 (100). Anal. calc. for $C_{29}H_8F_{20}O_2P_2$: C 41.95, H 0.97; found: C 41.78, H 1.11.

The ligands (+)-(1*S*,2*S*)-**7** and (–)-(1*R*,2*R*)-**7** were obtained by the same procedure using enantiomerically pure cyclopentanediol. (+)-(1*S*,2*S*)-**7**: $[\alpha]_D^{20} = +58$ ($c = 1.6$, $CHCl_3$). (–)-(1*R*,2*R*)-**7**: $[\alpha]_D^{20} = -59$ ($c = 1.6$, $CHCl_3$).

3. *Complexes* **8–12**. *(η^6-Benzene)bis(trimethoxyphosphine)carbonylchromium* (**8**). A soln. of [Cr(benzene)$(CO)_3$] (0.640 g, 2.99 mmol) and $P(OMe)_3$ (2.5 ml, 18 mmol) in benzene (130 ml) was placed into a photoreactor fitted with a fritted gas inlet. N_2 was passed through the soln. of 15 min. Maintaining a slow gas stream, the soln., kept at 15°, was then irradiated with a 125-W high-pressure Hg lamp using a *Pyrex* filter. After 2.5-h irradiation, IR indicated a product with a single absorption in the CO stretching region. The orange soln. was filtered and taken to dryness. The crude product was taken up in warm hexane. Slow cooling to –78° precipitated orange crystals (0.973 g, 79%). IR and ^1H-NMR indicated the very air-sensitive product to be **8** accompanied by 4% of the dicarbonyl monophosphite complex.

Data of **8**: M.p. 100–101°. IR (CH_2Cl_2): 2944*m*, 2836*w*, 1819v*s*, 1439*w*, 1178*w*, 1021v*s*. IR (THF): 1832v*s*. ^1H-NMR (400 MHz, C_6D_6): 4.58 (*t*, $J = 2.8$, 6 H); 3.51 (*dd*, $J = 5.5, 5.1$, 18 H). ^{31}P-NMR (162 MHz, C_6D_6): 219.45 (*s*). MS: 406 (19), 300 (37), 254 (14), 207 (14), 177 (22), 176 (100), 175 (11), 161 (17), 131 (18), 130 (13), 93 (61), 78 (17), 63 (27), 52 (39), 47 (10). Anal. calc. for $C_{13}H_{24}CrO_7P_2$: C 38.43, H 5.95; found: C 38.27, H 5.94.

General Procedure for **9–12**. A soln. of equimolar quantities of [Cr(benzene)$(CO)_3$] and the bidentate ligand (**4**, **5**, **6**, or **7**) in benzene or toluene (50 ml/mmol complex) was placed into a photoreactor fitted with a fritted gas inlet. N_2 was passed through the soln. for 15 min. Maintaining a slow gas stream, the soln., kept at 15°, was then irradiated with a 125-W high-pressure Hg lamp using a *Pyrex* filter. The reaction was followed by TLC and/or IR and was stopped, when all of the starting material had been consumed. At this stage, the IR in the ν(CO) region showed a single band. Concentration of the reaction mixture yielded the crude product.

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[2]) Alternatively, $(C_6F_5)MgBr$ may be efficiently prepared from C_6F_5Br and EtMgBr [36].

(η^6-Benzene)[trans-*1,2-bis(dimethoxyphosphinoxy)cyclopentane]carbonylchromium* (**9**). This complex was prepared with ligand *rac*-**4** (1.70 g, 5.93 mmol). The reaction was complete after 4 h of irradiation. The crude product was dissolved in Et_2O and filtered through Al_2O_3. Concentration and recrystallization from Et_2O afforded complex **9** as yellow solid (1.83 g, 68%). M.p. 104–106°. IR (THF): 1829v*s*. IR (hexane): 1848*s*, 1837*s*, 1460v*s*, 1380v*s*, 1125v*s*, 1075*s*, 1025*s*, 725*s*. ^{1}H-NMR (400 MHz, C_6D_6): 4.90–4.99 (*m*, 1 H); 4.67 (*t*, $J = 2.6$, 6 H); 4.36–4.45 (*m*, 1 H); 3.69 (*d*, $J = 10.7$, 3 H); 3.58 (*d*, $J = 10.3$, 3 H); 3.57 (*d*, $J = 11.0$, 3 H); 3.53 (*d*, $J = 9.9$, 3 H); 1.80–1.96 (*m*, 2 H); 1.55–1.75 (*m*, 2 H); 1.28–1.44 (*m*, 2 H). ^{13}C-NMR (50 MHz, C_6D_6): 243 (*t*, $J = 31$, CO); 86.4 (arom. C); 80.2–80.4 (CHO); 50.4–51.5 (CH_3O); 31.9–32.1 (CH_2); 20.4 (CH_2). ^{31}P-NMR (C_6D_6, 162 MHz): 219.15 (*AB*(*d*), $J = 91$); 217.29 (*AB*(*d*), $J = 91$). MS: 444 (4), 338 (25), 192 (55), 161 (38), 131 (35), 114 (57), 93 (100), 78 (90), 67 (53), 52 (73). Anal. calc. for $C_{16}H_{26}CrO_7P_2$: C 43.25, H 5.85; found: C 43.18, H 5.93.

*(η^6-Benzene)[(1*S*,2*S*)-bis(difluorophosphinoxy)cyclopentane]carbonylchromium* (**10**). This complex was prepared with ligand (1*S*,2*S*)-**5** (1.192 g, 5.0 mmol). The reaction was complete after 1.5 h of irradiation. The mixture was concentrated and then purified by flash chromatography. Recrystallization of the gummy product from Et_2O/hexane at −78° precipitated pale yellow crystals. The supernatant was removed by syringe and the product washed with cold hexane.

*Data of (1*S*,2*S*)-***10** (0.899 g, 45%). M.p. 180° (dec.). $[\alpha]_D^{20} = -61$ ($c = 2.1$, CH_2Cl_2). IR (THF): 1874v*s*. IR (hexane): 1892*s*, 1110*w*, 1080*w*, 880*m*, 820*m*, 800*m*. ^{1}H-NMR (400 MHz, C_6D_6): 4.88–4.97 (*m*, 1 H); 4.55 (*t*, $J = 2.8$, 6 H); 4.50–4.62 (*m*, 1 H); 1.55–1.67 (*m*, 2 H); 1.34–1.49 (*m*, 2 H); 0.96–1.06 (*m*, 2 H). ^{31}P-NMR (162 MHz, C_6D_6): 214.44 (*tAB*(*d*), $J = 1221, 91$); 212.57 (*tAB*(*d*), $J = 1221, 91$). Anal. calc. for $C_{12}H_{14}CrF_4O_3P_2$: C 36.38, H 3.56; found: C 36.56, H 3.56.

(η^6-Benzene){ trans-*1,2-bis{bis[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]phosphinoxy}cyclopentane}carbonylchromium* (**11**). This complex was prepared with ligand *rac*-**6** (1.90 g, 2.29 mmol). The mixture was irradiated for 3 h, filtered over *Celite* and concentrated. The crude product was recrystallized from toluene/hexane at −78° to give **11** (1.90 g, 84%) as yellow powder. M.p. 128–130°. IR (THF): 1865v*s*. IR (CH_2Cl_2): 1854v*s*, 1449*m*, 1367*s*, 1286*s*, 1232v*s*, 1201v*s*, 1107v*s*, 1084*s*, 882*s*, 872*s*, 820*m*, 786*s*. ^{1}H-NMR (200 MHz, C_6D_6): 5.06–5.38 (*m*, 3 H); 4.84–5.06 (*m*, 1 H); 4.77 (*t*, $J = 2.3$, 6 H); 4.40–4.63 (*m*, 2 H); 1.50–1.80 (*m*, 2 H); 1.10–1.40 (*m*, 4 H). ^{31}P-NMR (81 MHz, C_6D_6): 213.0 (*AB*(*d*), $J = 80$); 213.5 (*AB*(*d*), $J = 80$). MS: 882 (85), 821 (15), 731 (15), 647 (45), 600 (75), 517 (10), 449 (35), 433 (45), 386 (25), 365 (35), 333 (23), 277 (10), 217 (15), 149 (20), 129 (20), 91 (60), 78 (20), 67 (100). Anal. calc. for $C_{24}H_{18}CrF_{24}O_7P_2$: C 29.17, H 1.84; found: C 29.25, H 1.91.

(η^6-Benzene){ trans-*1,2-bis[bis(pentafluorophenyl)phosphinoxy]cyclopentane}carbonylchromium* (**12**). The complex was prepared with the ligand *rac*-**7** (1.50 g, 1.80 mmol). A product of low solubility formed during irradiation (7 h). Addition of CH_2Cl_2, filtration over *Celite*, and evaporation of volatiles under vacuum gave **12** as orange solid (1.54 g, 86%). Recrystallization from hot toluene (120 ml/g of complex) gave orange crystalline material. M.p. 212° (dec.). IR (THF): 1868v*s*. IR (CH_2Cl_2): 1862*s* (br.), 1640*m*, 1517*s*, 1466v*s*, 1422*m*, 1377*m*, 1088*s*, 976*s*. ^{1}H-NMR (200 MHz, (D_6)acetone): 4.84 (*t*, $J = 2.6$, 6 H); 4.52–4.74 (*m*, 1 H); 3.94–4.16 (*m*, 1 H); 1.40–2.00 (*m*, 6 H). ^{31}P-NMR (81 MHz, CD_2Cl_2): 178.4 (*AB*(br. *d*), $J = 53$); 167.2 (*AB*(br. *d*), $J = 53$). MS: 882 (60), 747 (40), 517 (20), 448 (35), 383 (25), 382 (25), 365 (60), 129 (20), 78 (80), 67 (100). Anal. calc. for $C_{36}H_{14}CrF_{20}O_3P_2$: C 43.75, H 1.43; found: C 44.38, H 1.80.

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