Cooksey by the mercuration of tri-*tert*-butylbenzene.[29]

ESR Spectroscopy. ESR spectra were recorded by using a Varian E4 or E109 spectrometer, fitted with a 500-W high-pressure mercury arc that was focused on the cavity and provided with neutral density (metal gauze) and glass (soda and Pyrex) filters.

Mercury trifluoroacetate (ca. 70 mg) was added to TFAH (1.3 cm^3) in a Suprasil ESR tube to give a saturated solution at room temperature. This was cooled to 262 ± 1 K, just above the freezing point of TFAH, and dissolved oxygen was removed by bubbling nitrogen through the solution for 5 min. A solution of the substrate (ca. 1 mg) in a minimum volume of TFAH or dichloromethane was added, and the solution was degassed for a further 1 min and then transferred to the precooled ESR cavity.

(29) Ditto, S. R.; Card, R. J.; Davis, P. D.; Neckers, D. C. *J. Org. Chem.* **1979**, *44*, 894-896. Huffman, J. C.; Nugent, W. A.; Kochi, J. K. *Inorg. Chem.* **1980**, *19*, 2749-2755.

Acknowledgment. We thank Dr. J. E. Anderson and Mr. C. J. Cooksey for their gift of samples and Dr. S. N. Yazdi for carrying out the work on the mercuration of anthracene. This work was supported by the SERC.

Efficient Synthesis of Substituted Derivatives of (Naphthalene)chromium(0) Carbonyls

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Tricarbonyl(η^6-1,4-epoxy-1,2,3,4-tetrahydronaphthalene) complex is a source of "protected" naphthalene for the indirect synthesis of Cr(η^6-naphthalene)$(CO)_2$L complexes, which can then be used in arene-exchange experiments. Experiments are reported for when L is a chiral 1,3,2-dioxaphospholane made by condensation of a chiral diol and $PPhCl_2$. Direct photolysis reactions of these ligands with Cr(η^6-naphthalene)$(CO)_3$ gives the substituted complexes in very poor yield (<3%). In contrast, photolysis reactions with the 1,4-epoxy-1,2,3,4-tetrahydronaphthalene complexes proceed in good (ca. 60–65%) yields, and subsequent dehydration by HBF_4 and BF_3 (ca. 50–65% yields) gives the substituted naphthalene complexes in an overall yield of 30–40% from the tricarbonyl. It is possible to exchange the naphthalene with monoarenes, though poor selectivity is observed in ligand-exchange experiments of the chiral naphthalene complexes with prochiral arenes.

Naphthalene complexes of the transition metals are an important subgroup of the metal arenes.[1] The naphthalene ligand or any other polyaromatic ligand is usually thermodynamically susceptible to exchange reactions with monoarenes,[2] and because of facile η^6 to η^4 ring slippage reactions, naphthalene is typically also kinetically quite labile.[4] This reactivity can be very useful, as demonstrated by the extensive chemistry of $Cr(CO)_3$(η^6-naphthalene) in stoichiometric[5] or catalytic[6] applications.

The utility of the naphthalene ligand is, however, limited because the very reactivity of the naphthalene ligand precludes many high-energy thermal or photolytic synthetic techniques. Thus, there are no convenient routes to potentially important substituted $Cr(CO)_2L(\eta^6$-naphthalene) derivatives. It is certainly true that photolytic substitution of a monoarene tricarbonyl complex proceeds quite smoothly in many cases,[7] but reports of such substitution reactions with related polyaromatic complexes[8] are quite uncommon and we infer from those papers that the yields are low despite arduous experimental methods. This may well be because the extended aromatic system alters the chromophore[9] to drive reactions other than CO expulsion, such as arene activation or cleavage.

In this paper, we report an efficient and, we believe, more generally applicable route to such substituted naphthalene complexes using the simple monoaromatic ligand, 1,4-epoxy-1,2,3,4-tetrahydronaphthalene, **1** (available commercially or from the Diels–Alder reaction

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransitionmetal Chemistry*, 2nd ed.; University Science: Mill Valley, CA, 1987.

(2) Connor, J. A.; Martinho-Simoes, J. A.; Skinner, H. A.; Zafarani-Moattar, M. T. *J. Organomet. Chem.* **1979**, *179*, 331.

(3) An interesting exception is provided by work involving η^4-arene systems, where the conjugated naphthalene is *preferred*: Leong, V. S.; Cooper, N. J. *Organometallics* **1988**, *7*, 2058.

(4) Kündig, E. P.; Perret, C.; Spichiger, S.; Bernardinelli, G. *J. Organomet. Chem.* **1985**, *286*, 183.

(5) (a) Brocard, J.; Lebibi, J.; Pelinski, L.; Mahmoudi, M. *Tetrahedron Lett.* **1986**, *27*, 6325. (b) Uemura, M.; Kobayashi, T.; Minami, T.; Hayashi, Y. *Tetrahedron Lett.* **1986**, *27*, 2479. (c) Uemura, M.; Minami, T.; Hirotsu, K.; Hayashi, Y. *J. Org. Chem.* **1989**, *54*, 469.

(6) (a) Bland, W. J.; Davis, R.; Durrant, J. L. A. *J. Organomet. Chem.* **1985**, *280*, 95. (b) Tucker, J. R.; Riley, D. P. *J. Organomet. Chem.* **1985**, *279*, 49.

(7) (a) Strohmeier, W.; Hellmann, H. *Chem. Ber.* **1963**, *96*, 2859. (b) Jaouen, G.; Howell, J. A. S.; Tirvengadum, M.-C.; McArdle, P.; Cunningham, D. *J. Organomet. Chem.* **1989**, *370*, 51. (c) Leong, V. S.; Cooper, N. J. *Organometallics* **1987**, *6*, 2000. (d) Jackson, W. R.; Rae, I. D.; Wong, M. G. *Aust. J. Chem.* **1984**, *36*, 1563. (e) Semmelhack, M. F.; Seufert, W.; Keller, L. *J. Organomet. Chem.* **1982**, *226*, 183. (f) Dabard, R.; Jaouen, G.; Simonneaux, G.; Cais, M.; Kohn, D. H.; Lapid, A.; Tartarsky, D. *J. Organomet. Chem.* **1980**, *184*, 91. (g) Andrianov, V. G.; Struchkov, Yu, T.; Baranetzkaya, N. K.; Setkina, V. N.; Kursanov, D. N. *J. Organomet. Chem.* **1975**, *101*, 209. (h) Jaouen, G.; Dabard, R. *J. Organomet. Chem.* **1974**, *72*, 377.

(8) (a) Cais, M.; Kaftory, M.; Kohn, D. H.; Tartarsky, D. *J. Organomet. Chem.* **1980**, *184*, 103. (b) Kaftory, M. *Acta Crystallogr.* **1980**, *B36*, 2971. (c) Cais, M.; Fraenkel, D.; Weidenbaum, K. *Coor. Chem. Rev.* **1975**, *16*, 227.

(9) (a) Armstrong, B. A.; Mahaffy, C. A. L.; Radzykewysz, D. T.; Rawlings, J. *Abstracts of Papers*, 199th Meeting of the American Chemical Society, Boston, MA; American Chemical Society: Washington, DC, 1990; INOR 483. (b) Armstrong, B. M.; Bowen, M. E.; Clark, M. L.; Foley, B. L.; Hamilton, J. B.; Mahaffy, C. A. L.; Rawlings, J.; Starr, T. R. *Inorg. Chim. Acta* **1990**, *170*, 37.

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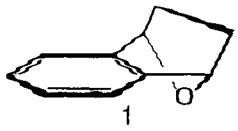
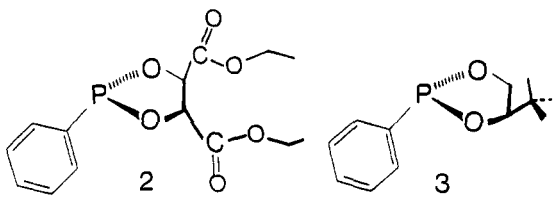


1

of furan and benzyne followed by hydrogenation[10]), as a source of "protected naphthalene". This is a novel approach to organometallic synthesis for, while protecting group strategies are a well-established principle in organic synthesis (even transition-metal reagents have been used to decrease the reactivity of π-systems toward electrophilic attack), we are aware of no other instances where a functional group is utilized in transition-metal organometallic chemistry for the sole purpose of protecting some functionality. This work complements our studies of the simple tricarbonyl derivative of epoxynaphthalene[11] that reacts as a polyfunctional chromium arene complex with significant potential in organic synthesis.[12] Our successful synthesis of substituted naphthalene complexes permits the preliminary study of the utility of chiral phosphorus ligands in asymmetric induction of the coordination of achiral arenes.

Results and Discussion

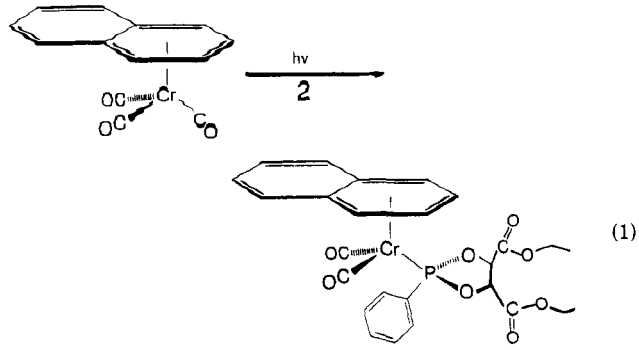
The chiral dioxaphospholanes for this study, derived from diethyl tartrate and (2*R*)-3,3-dimethyl-1,2-butanediol (*tert*-butylethylene glycol[13]), are synthesized in fair yield (55% and 43% after purification by distillation) by the condensation of the appropriate diol and $PhPCl_2$ in the presence of pyridine.[14] Diethyl tartrate is a homochiral diol, and therefore, only a single stereoisomer, **2**, is formed



2 3

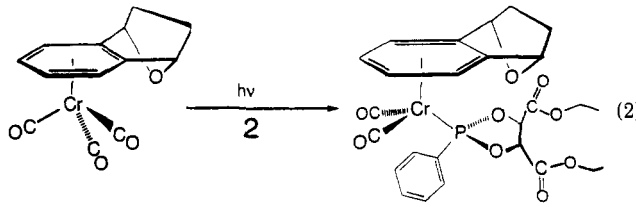
in the phosphorus product; inversion at the phosphorus generates the same compound. The ^1H NMR spectrum can be completely assigned, including the presence of a characteristic split resonance for the CH_2 protons of the ethyl group cis to the phenyl group. There are two stereoisomers possible with products derived from the monosubstituted diol, but only a single one, **3**, is formed, with the *tert*-butyl and the phenyl group mutually trans about the heterocycle.

It is indeed possible to synthesize substituted chromium naphthalene derivatives of **2** directly via photolysis in the presence of the ligand with $Cr(CO)_3(\eta^6\text{-}C_{10}H_8)$ (eq 1). However, the yields of the reactions are extremely low, about 2–3% after the required purification by chromatography. The materials are red oils and are identical with those obtained in analytically pure form via the indirect route described below.



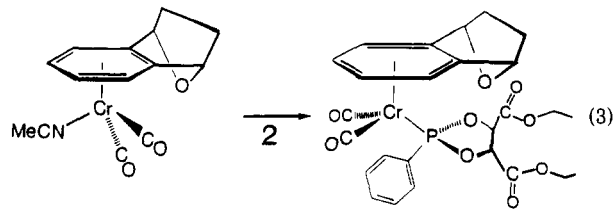
(1)

Synthesis of Substituted Naphthalene Complexes by a Protected Naphthalene Route. The epoxynaphthalene complex undergoes photolysis reactions in the manner expected for a monoarene complex (shown for **2** in eq 2). Depending on the dioxaphospholane, irradiation



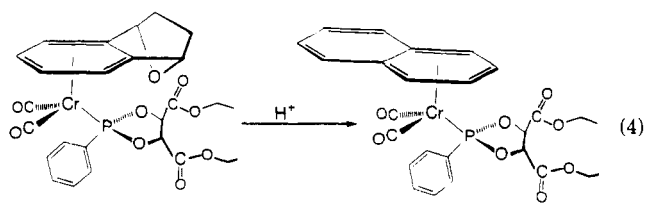
(2)

through either quartz or Pyrex of a tetrahydrofuran (THF) solution of the tricarbonyl and a slight excess of the ligands gives, after purification by column chromatography, the substituted complexes in ca. 64% yield. The photolytic synthesis with **3** is accompanied by a slight (ca. 2%) amount of epimerization at the phosphorus.[15] The complexes can also be made indirectly through a thermally labile acetonitrile complex, $Cr(\eta^6\text{-}C_{10}H_{10}O)(CO)_2(MeCN)$, which is synthesized by irradiation of the tricarbonyl in hexanes/MeCN (eq 3).



(3)

The dehydration of the substituted epoxynaphthalene complexes requires acid reagents that are selective for the epoxynaphthalene over the dioxaphospholane. Fortunately, the phosphorus heterocycle is quite stable when coordinated to chromium, and therefore, dehydration with either HBF_4 or BF_3 gives the substituted naphthalene complexes as red tars after chromatographic purification (eq 4). The overall yields, starting from the tricarbonyl complex, are in the range of 30–45%, clearly superior to those for the direct route.



(4)

The presence of an achiral arene and metal coordinated to a chiral phosphorus ligand creates diastereotopic sites on the arene and the metal. This is reflected in the NMR

(10) (a) Wittig, G.; Pohmer, L. *Chem. Ber.* **1956**, *89*, 1334. (b) Fieser, L. F.; Haddadin, M. J. *Can. J. Chem.* **1965**, *43*, 1599.

(11) Compound **1** will be referred to trivially in this paper as "epoxynaphthalene". The corresponding 1,4-epoxy-1,2-dihydronaphthalene compound is also available and is the subject of other experiments in our laboratories.

(12) Nirchio, P. C.; Wink, D. J. Submitted for publication.

(13) Guetté, J.-P.; Spassky, N. *Bull Chim. Soc. Fr.* **1972**, 4217. Note that all subsequent syntheses and spectroscopic data are merely indicative of *diastereoselection*, and therefore, the results are as valid as if racemic or optically impure diol was in use.

(14) Richter, W. J. *Phosphorus Sulfur Relat. Elem.* **1981**, *10*, 395.

(15) Mislow, K. *Trans. N.Y. Acad. Sci.* **1973**, *35*, 227.

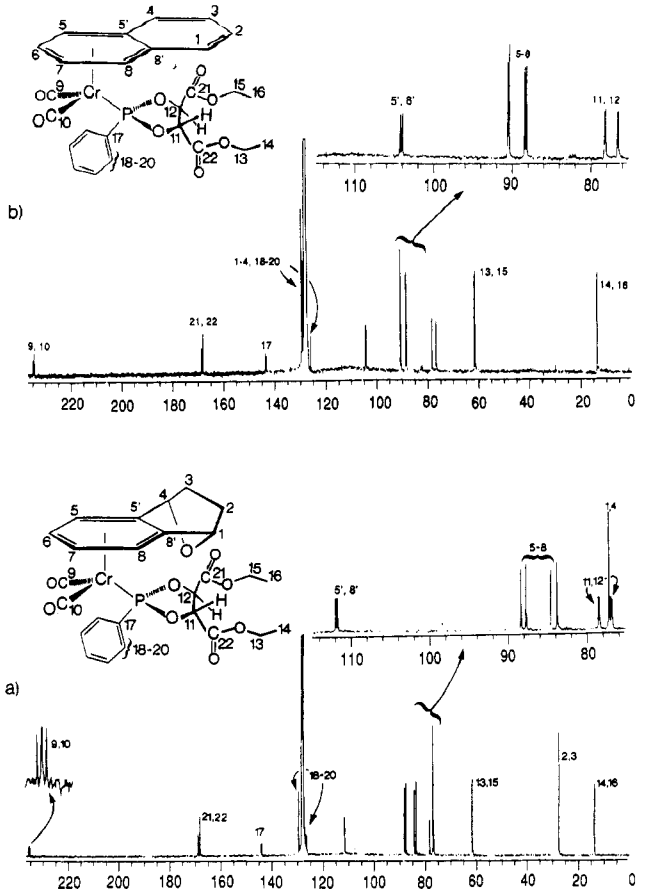


Figure 1. 75.453-MHz ^{13}NMR spectrum of the complexes of **2** and (a) $Cr(CO)_2(\eta^6\text{-}C_{10}H_{10}O)$ and (b) $Cr(CO)_2(\eta^6\text{-}C_{10}H_8)$. Note that the atom numbering for naphthalene has been done to be consistent with that of the epoxynaphthalene parent.

spectra of the epoxynaphthalene and the naphthalene complexes. Two examples for the compounds containing the dicarbethoxy-substituted ligands are shown in Figure 1. The CO ligands are now inequivalent, as are the carbons of the coordinated ring of the arene; the splitting observed in all cases is certainly due to chemical shift differences and not spin–spin coupling with phosphorus, which is expected to be negligible.[16] The differences between pairs of diastereotopic sites are consistently larger for the epoxynaphthalene derivatives when compared to the naphthalene derivatives. We speculate that this is due to a change in the preferred conformation of the $Cr(CO)_2L$ group with respect to the arene. However, there is considerable ambiguity in the literature regarding the preferred location of the $Cr(CO)_2L$ fragment with respect to a substituted arene,[6] and in the absence of a crystal structure (recall that all four compounds in question are oils at room temperature), no further conclusions can be developed.

Arene-Ligand-Exchange Experiments. The first efficient preparation of a chiral chromium naphthalene complex permits an initial study of the utility of auxiliary ligands in asymmetric induction in substrate coordination. Substrate π-face coordination can, of course, be controlled in other ways. The groups of Uemura,[5b,c] Brocard,[5a] and (for cyclic alcohols such as tetralol) Jaouen[17] have shown that a chiral alcohol on an α,ortho-disubstituted arene can be used to direct one diastereoface of an arene onto the metal. The groups of Davies and Heppert/Aubé have also shown that a chiral amine or ether on an arene serves well as a directing group in lithiation experiments.[18] Finally, Howell and co-workers have reported that chiral phosphorus ligands are useful as auxiliaries in the separation of isomers that vary according to π-face complexation to chromium[7b] using a strategy where the phosphorus ligand is attached *after* the prochiral arene. However, we are aware of no reports of experiments concerning the addition of a prochiral arene to a complex containing a chiral phosphorus ligand in an asymmetric induction strategy[19] analogous to that developed by Birch for the synthesis of chiral diene iron complexes through an intermediate chiral enone derivative.[20]

Table I. Results of Arene-Exchange Experiments

arene	yield,[a] %	ratio of diastereomers[b]
o-(trimethylsilyl)benzaldehyde	10	0.76:1
o-methylbenzyl alcohol	57	0.88:1
o-(trimethylsilyl)anisole	44	0.63:1
o-(trimethylsilyl)benzyl alcohol	51	0.83:1
m-methylbenzyl alcohol	57	0.92:1
2-biphenylmethanol[c]	46	0.83:1

[a] All yields are of spectroscopically clean mixtures of diastereomers obtained after chromatography. [b] The ratio of diastereomers in the isolated product was determined by integration of the ^{31}P or ^{1}H NMR spectrum. [c] There is also a structural isomer present, with the $Cr(CO)_2L$ group on the monosubstituted ring.

There are several excellent studies of the exchange of reactions of arene ligands attached to the chromium tricarbonyl fragment.[21] However, we know of only one report, by Semmelhack and co-workers,[7e] of an attempt to exchange the arene in a substituted complex. They observed exchange of monoarenes such as benzene for one such as xylene, but only slowly, even at 200 °C. The metal–arene interaction is presumably much stronger because the less π-acidic L makes the metal to arene bond stronger. The arene should be more difficult to replace, even with Lewis base assistance.

We find that the naphthalene complex containing the *tert*-butyldioxaphospholane ligand is, indeed, completely ineffective in arene-exchange experiments. But the naphthalene in the dicarbethoxy derivative can be displaced by monoarenes, in some cases in fair yields (Table I). We speculate that this difference in reactivity with the two different dioxaphospholanes is because a carbethoxy group, but not a *tert*-butyl group, can coordinate to the metal to speed up the departure of the naphthalene. However, there are no cases where asymmetric induction occurs to any meaningful extent. This may be because the incoming prochiral arene attacks from the side opposite the chiral auxilary or it may be due to the free rotation of the auxiliary about the Cr–P bond to swing the chiral directing groups away from the metal. Further experiments, using more elaborate phosphorus ligands, are apparently required.

(16) Desroby, V.; Kündig, E. P. *Helv. Chim. Acta* **1981**, *64*, 1288.
(17) Jaouen, G.; Meyer, A. *J. Am. Chem. Soc.* **1975**, *97*, 4667.
(18) (a) Blagg, J.; Davies, S. G.; Goodfellow, C. L.; Sutton, K. H. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1805. (b) Heppert, J. A.; Aubé, J.; Thomas-Miller, M. E.; Milligan, M. L.; Takusagawa, F. *Organometallics* **1990**, *9*, 727.
(19) Note the requirement that the asymmetric induction be achieved kinetically since the coordination of the monoarene is likely to be irreversible.
(20) Birch, A. J.; Raverty, W. D.; Stephenson, G. R. *Organometallics* **1984**, *3*, 1075.
(21) Leading references are found in the studies of Traylor, including: (a) Traylor, T. G.; Stewart, K. J. *J. Am. Chem. Soc.* **1986**, *108*, 6977. (b) Traylor, T. G.; Stewart, K. J.; Goldberg, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 4445.

Conclusion

Many metal ligand environments possess reactivity that is quite troublesome in some situations. This may simply be because a given metal–ligand bond is thermally or photochemically too reactive or because the activation of a substrate by metal directs reactions to the substrate, not the metal. These problems, as in organic synthesis, can in principle be overcome very easily through the use of the appropriate protecting groups. This report is, to our knowledge, the first such explicit example of a protecting group in organotransition-metal chemistry; we anticipate that several other examples of such indirect yet more efficient syntheses will be developed.

Experimental Section

General Considerations. All elemental analyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, NY. Tricarbonyl(η^6-1,4-epoxy-1,2,3,4-tetrahydronaphthalene)-chromium[11] and tricarbonyl(η^6-naphthalene)chromium were synthesized by refluxing the ligand with chromium hexacarbonyl in dibutyl ether in the presence of a small amount of added THF. Diethyl ether (Fisher) and tetrahydrofuran (Fisher) were dried over potassium benzophenone and distilled. Silica gel for chromatography (Aldrich) was 230–400 mesh and was used as received.

Direct Photosubstitution of Tricarbonyl(η^6-1,4-epoxy-1,2,3,4-tetrahydronaphthalene)chromium with 2, Dicarbonyl[(4*R*,5*R*)-4,5-dicarbethoxy-2-phenyl-1,3,2-dioxaphospholane](η^6-1,4-epoxy-1,2,3,4-tetrahydronaphthalene)-chromium(0). A mixture of $Cr(CO)_3(\eta^6$-$C_{10}H_{10}O)$ (6.6 g, 23 mmol) and **2** (8.6 g, 27 mmol) in 250 mL of THF was prepared in a Pyrex Schlenk flask. The mixture was irradiated, with a nitrogen purge, for 5 h by using an adjacent mercury lamp. The solvent was removed from the canary yellow solution in vacuo, and then the crude product was purified by chromatography on silica using 5:1 pentane:acetone to give 8.4 g (15 mmol, 64%) of spectroscopically pure product as a yellow oil. Samples for elemental analysis were prepared by an additional chromatographic purification with 3:1 pentane:ether IR 1920 and 1869 (ν_{CO}), 1817 cm^{-1} (ν_{CO_2Et}). ^{1}H NMR δ 7.79 (2 H, t, *o*-C_6H_5); 7.08 (2 H, t, *m*-C_6H_5); 6.96 (1 H, t, *p*-C_6H_5); 5.16 (1 H, d, J_{HH} = 6.3 Hz, OC*H* cis to Ph); 5.05 (1 H, d of d, J_{HH} = 6.3, J_{PH} = 10.2 Hz, OC*H* trans to Ph); 5.00, 4.93 (1 H each, m, H^5, H^8), 4.66 (2 H, m, H^6, H^7); 4.74 (2 H, m, H^1, H^4); 3.92 (2 H, q, CH_2 trans to Ph); 3.60 (2 H, overlapping q's, CH_2 cis to Ph); 1.54 (2 H, m, exo H^2, H^3); 0.89 (ca. 2 H, m, endo H^2, H^3); 0.88 (ca. 3 H, t, CH_3 trans to Ph); 0.73 (3 H, t, CH_3 cis to Ph). ^{13}C NMR δ 236.1 (d, J_{PC} = 28.5 Hz, *C*O), 235.7 (d, J_{PC} = 26.9 Hz, *C*O); 169.1 (s, CO_2Et), 168.3 (d, J_{PC} = 7 Hz, CO_2Et); 144.3 (d, J_{PC} = 28 Hz, ipso-C_6H_5); 129.7, 128.5, 127.9 (*o*-, *m*-, *p*-C_6H_5); 111.9, 111.6 (C^5, C^8); 88.3, 87.6 (C^6, C^7); 84.5, 83.7 (C^5, C^8); 78.4 (d, J_{PC} = 11 Hz, *C*HCO$_2$R), 77.1 (C^1, C^4); 76.8 (d, J_{PC} = 9 Hz, *C*HCO$_2$R); 61.9, 61.6 (CH_2); 27.7 (C^2, C^3); 14.0, 13.8 (CH_3). ^{31}P NMR δ 263.1. Anal. Calcd for $C_{26}H_{27}CrO_9P$: C, 55.13%; H, 4.80%. Found: C, 55.79%; H, 4.82%.

[(2*R*,4*R*)-4-*tert*-Butyl-2-phenyl-1,3,2-dioxaphospholane]dicarbonyl(η^6-1,4-epoxy-1,2,3,4-tetrahydronaphthalene)chromium(0). A mixture of $Cr(CO)_3(\eta^6$-$C_{10}H_{10}O)$ (1.5 g, 5.3 mmol) and **3** (1.8 g, 8.0 mmol) in 40 mL of THF was prepared in a quartz Schlenk flask. Irradiation was done, in an ice–water bath and with a nitrogen purge, for 5 h by using an adjacent mercury lamp. The solvent was removed in vacuo, and then ethyl ether (40 mL) was added. The ether was removed, and the crude product was purified by chromatography on silica using toluene:hexanes in ratios increasing from 1:5 to 3:1 to give 1.6 g (3.3 mmol, 63%) of spectroscopically pure product as a yellow oil. Samples for elemental analysis were prepared by an additional chromatographic purification with 4:1 pentane:ether. IR 1917 and 1862 cm^{-1} (ν_{CO}). ^{1}H NMR δ 7.73 (2 H, t, *o*-C_6H_5); 7.19 (2 H, d, *m*-C_6H_5); 7.04 (1 H, t, *p*-C_6H_5); 4.68 (2 H, m, H^5, H^8), 4.51 (2 H, m, H^1, H^4); 4.36 (2 H, m, H^6, H^7); 3.74 (1 H, m, OCHBu^t); 3.58 (2 H, CH_2); 1.50 (2 H, m, exo H^2, H^3); 0.87 (2 H, m, endo H^2, H^3); 0.81 (s, CH_3). ^{13}C NMR δ 236.0 (d, J_{PC} = 13.4 Hz, *C*O), 235.6 (d, J_{PC} = 13.4 Hz, CO); 146.4 (d, J_{PC} = 23 Hz, ipso-C_6H_5); 129.2, 127.3, 126.6 (*o*-, *m*-, *p*-C_6H_5); 110.2, 109.8 (C^5, C^8); 86.5, 86.0 (C^6, C^7); 84.1 (d, J_{PC} = 10 Hz, *C*HCMe$_3$); 82.8, 82.2 (C^5, C^8); 77.0 (C^1, C^4); 66.5 (d, J_{PC} = 9 Hz, CH_2); 33.8 (*C*Me$_3$); 27.8 (C^2, C^3); 25.3 (CH_3). ^{31}P NMR δ 250.3. Anal. Calcd for $C_{24}H_{27}CrO_5P$: C, 60.24%; H, 5.69%. Found: C, 60.94%; H, 5.98%.

Synthesis via (Acetonitrile)dicarbonyl(η^6-1,4-epoxy-1,2,3,4-tetrahydronaphthalene)chromium(0) and Thermal Dioxaphospholane Exchange. A mixture of tricarbonyl(η^6-1,4-epoxy-1,2,3,4-tetrahydronaphthalene)chromium(0) (4.5 g, 16 mmol) and 20 mL of acetonitrile in 400 mL of a mixture of hexanes was placed in a photolysis apparatus, which was immersed in a salt water/ice bath at −10 °C. Irradiation for 4 h with using unfiltered radiation from a mercury vapor lamp gave a suspension of red solids. The solution was cooled to −20 °C, and the solution was decanted. The solids were dissolved in 80 mL of 1:1 ether:THF to give a red solution, which was decanted to a Schlenk tube. The solvent was removed in vacuo at 0 °C and (4*R*,5*R*)-4,5-dicarbethoxy-2-phenyl-1,3,2-dioxaphospholane (4.98 g, 16.0 mmol) in 50 mL of ether and 2 mL of THF were added. The mixture was stirred at room temperature for 48 h. The yellow solution was concentrated in vacuo to an oily residue and purified by chromatography on silica gel using 5:1 pentane:acetone to give, after removal of the eluant, 5.63 g of dicarbonyl [(4*R*,5*R*)-4,5-dicarbethoxy-2-phenyl-1,3,2-dioxaphospholane)](η^6-1,4-epoxy-1,2,3,4-tetrahydronaphthalene)chromium(0) (63%).

Dehydration Using HBF_4: [(2*R*,4*R*)-4-*tert*-Butyl-2-phenyl-1,3,2-dioxaphospholane]dicarbonyl(η^6-naphthalene)chromium(0). A 40-mL thick-walled flask was charged with 0.50 g (1.04 mmol) of the substituted epoxynaphthalene complex and 20 mL of ether. The mixture was deoxygenated with three freeze–thaw cycles, and then 100 μL of 50% HBF_4 in ether was added while the mixture was still frozen. The flask was reevacuated and then closed off. The solution gradually turned a deep red while it was stirred at room temperature for 64 h. The flask was opened to air and 2 mL of 2 M K_2CO_3 was added. After 10 min, the ether layer was separated, the aqueous layer was extracted with 3 × 10 mL of ether, and then the combined ether layers were dried with $MgSO_4$ before removal of the solvent. Purification by chromatography on silica gel with 3:1 pentane:ether gave 0.211 g of product (0.55 mmol, 52%) as a red oil. IR 1908 and 1853 cm^{-1} (ν_{CO}). ^{1}H NMR δ 7.48 (2 H, t, *o*-C_6H_5); 6.98 (3 H, m, *o*- and *m*-C_6H_5); 6.74 (2 H, m, H^2, H^3; H^1 and H^4 are obscured by solvent); 5.36 (2 H, m, H^5, H^8), 4.72 (2 H, m, H^6, H^7); 3.63 (1 H, m, OC*H*Bu^t); 3.51 (2 H, C*H*$_2$); 0.74 (s, CH_3). ^{13}C NMR δ 235.1 (overlapping d, *C*O), 145.6 (d, J_{PC} = 22 Hz, ipso-C_6H_5); 129.2, 127.3, 126.6 (C^1–C^4, *o*-, *m*-, *p*-C_6H_5); 104.1 (C^5, C^8); 89.4, 89.2 (C^6, C^7); 87.0, 86.8 (C^5, C^8); 84.0 (d, J_{PC} = 6 Hz, *C*HBu^t); 66.5 (d, J_{PC} = 9 Hz, CH_2); 33.8 (*C*Me$_3$); 25.37 (CH_3). ^{31}P NMR δ 248.0. Anal. Calcd for $C_{24}H_{25}CrO_4P$: C, 62.60%; H, 5.47%. Found: C, 63.24%; H, 5.77%.

Dehydration Using BF_3: Dicarbonyl[(4*R*,5*R*)-4,5-dicarbethoxy-2-phenyl-1,3,2-dioxaphospholane](η^6-naphthalene)chromium(0). A 40-mL thick-walled Schlenk tube equipped with a magnetic stir bar and a Teflon stopcock was charged with 1.0 g (1.8 mmol) of the substituted epoxynaphthalene complex and 15 mL of Et_2O. The mixture was deoxygenated with three freeze–pump–thaw cycles and then frozen in a liquid nitrogen bath; a 500-μL aliquot of BF_3·Et_2O was added and permitted to freeze before the vessel was reevacuated and closed off. The mixture gradually turned deep red while it was stirred at 50 °C for 16 h. The reaction was cooled to room temperature, opened to air, and quenched with 2 mL of 2 M K_2CO_3. The layers were separated, and the aqueous layer was extracted with 3 × 10-mL aliquots of ether. Purification by chromatography on silica with 3:1 pentane:ether as eluant gave 0.52 g of analytically pure product (0.95 mmol, 54%) as a red tar. IR 1912 and 1860 (ν_{CO}), 1745 cm^{-1} (ν_{CO_2Et}). ^{1}H NMR δ 7.53 (2 H, t, *o*-C_6H_5); 6.94 (2 H, t, *m*-C_6H_5); 6.85 (1 H, t, *p*-C_6H_5); 6.78 (2 H, d of d, H^2, H^3—the resonance for H^1, H^4 is obscured by C_6D_5H); 5.60, 5.54 (1 H each, m, H^5, H^8); ca. 5.0 (2 H, m, OC*H* cis and trans to Ph—overlapping with the following resonance); ca. 4.93 (2 H, m, H^6, H^7, overlapping with the previous resonance); 3.88 (2 H, q, CH_2 trans to Ph); 3.50 (2 H, overlapping q's, CH_2 cis to Ph); 0.83 (ca. 3 H, t, CH_3 trans to Ph); 0.64 (3 H, t, CH_3 cis to Ph). ^{13}C NMR δ 234 (overlapping d, $J_{PC} \approx$ 28 Hz, *C*O); 168.5 (δ, J_{PC} = 7 Hz, CO_2Et); 167.9 (s, CO_2Et); 143.1 (d, J_{PC} = 29 Hz, ipso-C_6H_5); 129–127 (C^1–C^4, *o*-, *m*-, *p*-C_6H_5); 104.6, 104.3 (C^5, C^8); 90.9, 90.7 (C^6, C^7); 88.5, 88.7 (C^5, C^8); 78.5 (d, J_{PC} = 11 Hz, *C*HCO$_2$R); 76.9 (d, J_{PC} = 9 Hz, *C*HCO$_2$R); 61.9,

61.6 (CH_2); 14.0, 13.7 (CH_3). ^{31}P NMR δ 261.4. Anal. Calcd for $C_{26}H_{25}CrO_8P$: C, 56.94%; H, 4.59%. Found: C, 57.62%; H, 4.66%.

Direct Photosubstitution of Tricarbonyl(η^6-naphthalene)chromium. A solution of $Cr(CO)_3(C_{10}H_8)$ (2.00 g, 7.57 mmol) and (4*R*,5*R*)-2-phenyl-4,5-dicarbethoxy-1,3,2-dioxaphospholane (3.39 g, 15.1 mmol) in 350 mL of pentane/80 mL of THF was prepared in a Schlenk tube and then transferred to a ultraviolet immersion photolysis apparatus. The apparatus was immersed in ice–water and a stream of N_2 was bubbled through the solution while the mixture was photolyzed with the mercury vapor lamp enclosed in a Vycor sleeve. After 1 h, the photolysis was halted and the mixture allowed to stir for 1.5 h. If the photolysis reaction were continued further, extensive decomposition occurred and all CO containing species were lost, as determined by IR spectroscopy. The red solution was removed by filtration, and the solvent was removed in vacuo. The residue was chromatographed on silica gel with 1:3 Et_2O:hexanes to remove the free phospholane followed by hexanes/benzene in the ratio 1:1 up to 1:4 to elute the substituted (naphthalene)chromium compound, which was isolated by evaporation of the solvent: 0.098 g, 2.8%. Spectroscopic and analytical information are given above.

Ligand-Exchange Reactions. A typical reaction is as follows: A 40-mL thick-walled flask was charged with complex (0.10 g, 0.18 mmol) and *o*-methylbenzyl alcohol (0.329 g, 2.7 mmol) and THF (146 μL). The mixture was subjected to three freeze–thaw cycles and then heated to 85 °C in vacuo overnight. The color changes from red to yellow as the reaction proceeds. Purification on silica gel using 2:1 pentane:ether and then 3:3:1.5 toluene:pentane:ethyl acetate gave 0.061 g of a yellow oil identified as a 5:6 mixture of diastereomers of dicarbonyl[(4*R*,5*R*)-4,5-dicarbethoxy-2-phenyl-1,3,2-dioxaphospholane)](η^6-*o*-methylbenzyl alcohol)chromium(0).

Synthesis of Chiral Dioxaphospholane Ligands. The synthesis of (4*R*,5*R*)-4,5-dicarbethoxy-2-phenyl-1,3,2-dioxaphospholane, **2**, was adapted from the procedure of Richter.[14] A 1-L three-necked round-bottomed flask was charged with 500 mL of dry diethyl ether, 25.1 mL of (+)-diethyl tartrate (27.6 g, 0.349 mol), and 28.2 mL of pyridine (27.6 g, 0.349 mol). The mixture was immersed in an ice–water bath and a solution of 18.9 mL of $PPhCl_2$ (25.0 g, 0.140 mol) in 100 mL of ether was added dropwise over 4 h while the reaction was mechanically stirred. The mixture was then allowed to warm slowly to room temperature overnight, with continuous stirring. The product (24 g, 55%) was collected as a colorless liquid after vacuum distillation (0.3 mmHg, 126 °C). ^1H NMR δ 7.48, 7.01 (5 H, m, C_6H_5); 5.14 (1 H, d, C*H* cis to phenyl—a 10% nOe develops in this signal when this ortho-proton resonance is irradiated); 4.90 (1 H, t, C*H* trans to phenyl, J_{P-H} = 7 Hz); 3.87 (2 H, 1, CH_2 trans to phenyl group), 3.59 (2 H, partially resolved q's, CH_2 cis to phenyl group—a ca. 1% nOe appears on the ortho protons when these are irradiated); 0.84, 0.70 (2 × 3 H, CH_3's). ^{13}C NMR δ 168.5, 168.0 (d's, J_{P-C} = 5 Hz, CO_2Et's); 142.8, (d, $^1J_{P-C}$ = 48 Hz, ipso-C of C_6H_5); 130.7, 129.1, 128.5 (*o*-, *m*-, and *p*-C of C_6H_5); 78.3, 77.6 (d's, J_{P-C} = 8 Hz, $CHCO_2Et$'s); 62.0, 61.7 (CH_2's); 13.9, 13.7 (CH_3's). ^{31}P NMR δ 182.7.

A similar procedure was employed for (2*R*,4*R*)-4-*tert*-butyl-2-phenyl-1,3,2-dioxaphospholane, **3**, with 11.7 mL of pyridine (11.4 g, 0.144 mol), (2*R*)-3,3-dimethyl-1,2-butanediol (6.0 g, 0.050 mol), and $PPhCl_2$ (8.62 g, 0.48 mol). After the solution was filtered from the solids, the solvent was removed and 9.53 g of the crude product was obtained (ca. 0.042 mol, 80–85% yield). This was distilled to give 4.77 g (0.021 mol, 43% yield) of spectroscopically pure material. ^1H NMR δ 7.41, 7.12 (5 H, m, C_6H_5); 3.63 (m, H, C*H*—an nOe is detected in the ortho protons of the aryl when this resonance is irradiated, supporting the assignment of a mutually trans arrangement of the *tert*-butyl and phenyl groups), 3.51 (m, 2 H, CH_2); 0.75 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR δ 144.8 (d, $^1J_{P-C}$ = 46 Hz, ipso-C of C_6H_5); 129.8, 128.6, 128.4 (*o*-, *m*-, and *p*-C of C_6H_5); 84.2 (d, J_{P-C} = 9 Hz, $CHBu^t$); 65.3 (d, J_{P-C} = 9 Hz, CH_2); 33.6 ($C(CH_3)_3$); 25.4 ($C(CH_3)_3$). ^{31}P NMR δ 165.8.

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Note Added in Proof. Ligand protection has also been employed in the efficient synthesis of technetium thiolate complexes: Bryson, N.; Lister-James, J.; Jones, A. G.; Davis, W. M.; Davison, A. *Inorg. Chem.* **1990**, *29*, 2948.