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Supplementary Material Available: A listing of observed and calculated structure factor amplitudes, ORTEP of the PPN⁺ cation

with the atomic labeling scheme, a complete listing of all bond lengths and angles for the cation, and tables of atomic positional coordinates and anisotropic thermal parameters for the cation (27 pages). Ordering information is given on any current masthead page.

Stereochemical Studies of the Carbon Dioxide Insertion Reactions into the Tungsten-Alkyl Bond

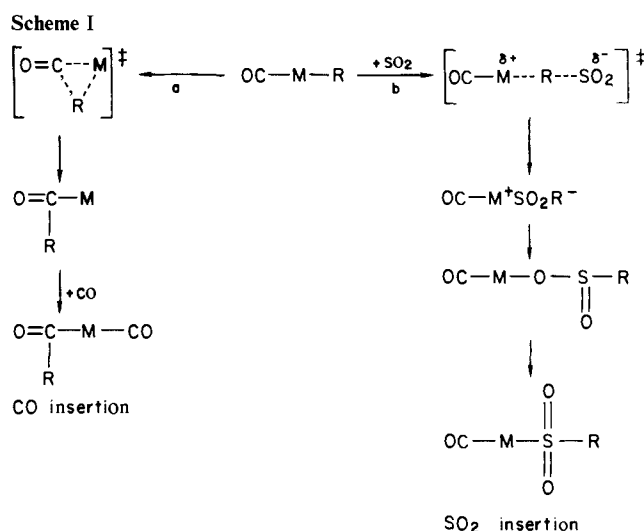
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Abstract: Unequivocal demonstration of the α -carbon stereochemistry in the carbon dioxide insertion reaction has been accomplished by the conversion of *threo*-W(CO)₅CHDCHDPh⁻ with CO₂ to *threo*-W(CO)₅O₂CCHDCHDPh⁻, indicating that a high degree of retention of configuration at the carbon was involved. A similar observation has been noted for the phosphine substituted derivative *threo-cis*-W(CO)₄[PMe₃]CHDCHDPh⁻ which reacts with carbon dioxide to afford *threo-cis*-W(CO)₄[PMe₃]O₂CCHDCHDPh⁻. For comparative purposes, migratory CO insertion induced by carbon monoxide transformed *threo*-W(CO)₅CHDCHDPh⁻ to *threo*-W(CO)₅C(O)CHDCHDPh⁻. Hence, *threo*-W(CO)₅CHDCHDPh⁻ undergoes both insertion of carbon monoxide and carbon dioxide to afford 1,1- and 1,2-addition products, respectively, with retention of configuration at the α -carbon atom.

Mechanistic pathways of CO- and SO₂-insertion reactions into metal-carbon bonds have been extensively investigated over the past decade.¹ Examination of the stereochemical fate of the metal center² as well as the α -carbon^{3,4} has demonstrated that (a) CO insertion occurs with retention of configuration at the α -carbon atom and inversion of configuration at the metal center and (b) SO₂ insertion occurs with inversion of configuration at the carbon center and retention of configuration at the metal fragment. These stereochemical studies for CO insertion are indicative of a concerted 1,2-migration of the alkyl group to coordinated CO followed by the saturation of the free coordination site by the incoming nucleophile, e.g., CO.⁵ On the other hand, an S_E2 mechanism with SO₂ attacking at the backside of the alkyl group is operative for SO₂ insertion. These two quite different reaction pathways are diagrammatically illustrated in Scheme I below.

Stereochemical investigations of the less well-studied carbon dioxide insertion reaction into metal-carbon bonds⁶ have thus far not been reported, and the available kinetic and structural data



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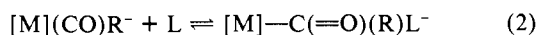
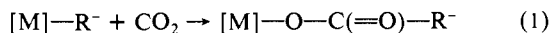
do not allow for a *definitive* assessment of the insertion process.⁷

In this paper, we wish to report on the stereochemistry at the α -carbon of the carbon dioxide insertion reaction into the tungsten-carbon bond. For convenience, we have chosen the [PNP][*cis*-W(CO)₄(L)(CHDCHDPh)] (L = CO and Me₃P) derivatives for these investigations since it is anticipated that the reaction pathway will be easily monitored by ¹H NMR spectroscopy⁸ and that the mechanistic analogy with other group 6 metal-alkyl and -aryl complexes will be maintained.⁹ An equally

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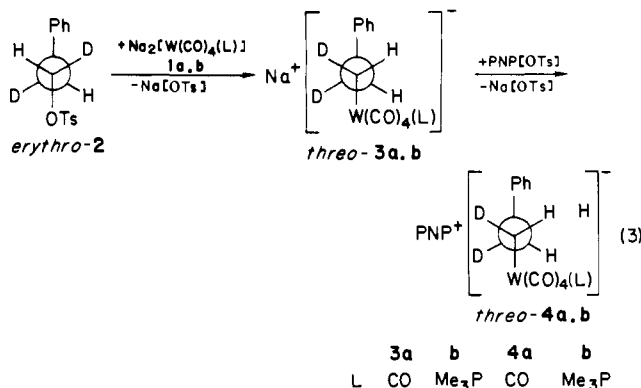
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important rationale for employing these particular metal complexes is the fact that these anionic metal substrates sustain both carboxylation and carbonylation reactions under similar conditions. Hence, these substrates offer the distinct opportunity for comparative stereochemical studies of reactions 1 and 2 by employing a common substrate.



Results and Discussion

Reaction of $Na_2[W(CO)_4L]$ ($L = CO$ for **1a**; $L = Me_3P$ for **1b**) with *erythro*-PhCHDCHDOTs (**2**) followed by cation exchange with PNP[OTs] in situ yields the configurationally stable PNP[*threo*- $W(CO)_4(L)$ (CHDCHDPh)] (**4a,b**) (eq 3) in the expected stereospecificity.^{3,8}



In the preparation of **4a**, the hydrogen-bridged compound $PNP[(\mu-H,D)\{W(CO)_3\}_2]$ (**5**)¹⁰ is found as a side product (10–20% yield according to the $\nu(CO)$ absorptions). This impurity is probably formed by β -H,D abstraction from the alkyl ligand. In THF solution, **4a** decomposes slowly even at $-10^\circ C$ to **5** and further uncharacterized species. The yield of the phosphine-substituted **4b** is only 34%, far below that of **4a** because it decomposes in solution rapidly to *cis*- $W(CO)_4(PMe_3)_2$ (**6**).¹¹ $PNP[(\mu-H,D)\{W(CO)_3\}\{W(CO)_4(PMe_3)\}]$ (**7**) might be an intermediate herein, as indicated by a weak absorption at 1928 cm^{-1} found in the IR spectra of THF solutions of **4b**. This infrared absorption corresponds to the strongest $\nu(CO)$ band reported for the $Et_4N[(\mu-H)\{Mo(CO)_3\}\{Mo(CO)_4(PMe_3)\}]$ derivative.¹²

Kinetic investigation of the 1,2-addition of carbon dioxide to tungsten-alkyl derivatives, *cis*- $RW(CO)_4L^-$ ($R = \text{alkyl group}$; $L = CO$ or PR_3), to provide metalcarboxylates has shown this reaction to obey a second-order rate law, first-order in anionic metal substrate and first-order in carbon dioxide.^{9,13,14} Carbon dioxide insertion into the $W-C$ bonds of **4a,b** proceeds with complete retention of configuration at the α -carbon center, within the limits of detection by 1H NMR spectroscopy. The reaction exhibits the previously established rate acceleration upon substitution (eq 4) of the metal center with a good donor ligand such as Me_3P .^{9,13} The side products **5** and **6** are formed from **4a** and **4b**, respectively, as described above. In addition, trace quantities of $W(CO)_6$ were detected, arising from the decomposition of the alkyl- or carboxylate-tungsten compounds.

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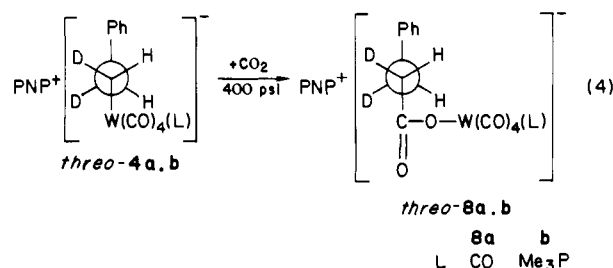
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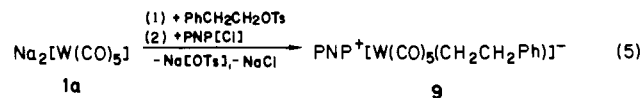
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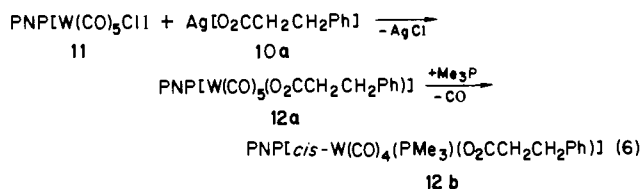
(14) The pseudo-first-order rate constant for the CO_2 insertion in $PNP[W(CO)_5(CHDCHDPh)]$ was determined as $2.03 \times 10^{-8}\text{ s}^{-1}$ ($t_{1/2} = 94.5\text{ h}$); for $PNP[W(CO)_4(PMe_3)(CHDCHDPh)]$, an approximate $t_{1/2}$ of 10 min was found ($T = 298\text{ K}$, solvent THF, $P(CO_2) = 400\text{ psi}$). Reaction was monitored in the $\nu(CO)$ region.



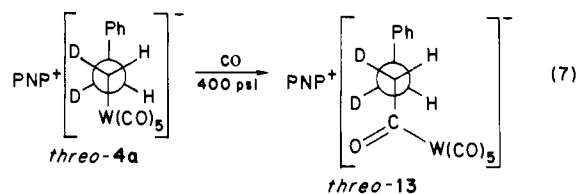
Characterization of the deuterated complexes **4a** and **8a,b** was aided by spectral comparisons with their nondeuterated analogues and with authentic samples prepared via alternative, more conventional routes. The phenethyl compound **9** was prepared in the same manner as **4a** (eq 5). The hydrocinnamate species **12a,b**



were synthesized by the reaction of silver 3-phenylpropionate (**10a**) with $PNP[W(CO)_5Cl]$ (**11**) which leads to **12a**, with subsequent thermal CO ligand substitution by Me_3P providing **12b**.¹⁵ In an analogous manner, **8a,b** were prepared from silver *threo*-2,3-di-deuterio-3-phenylpropionate (**10b**) and **11** (eq 6).



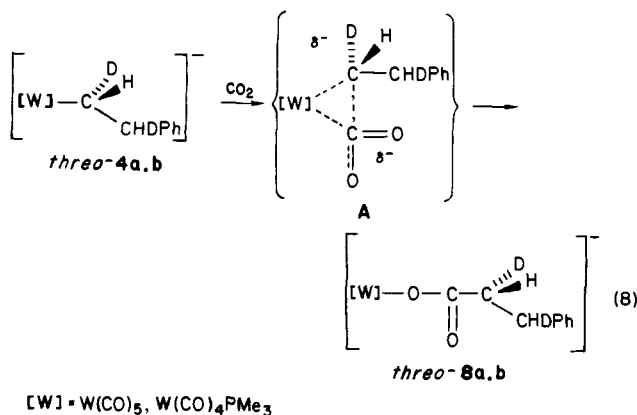
Isolation and characterization of the anionic tungsten-alkyl derivative $PNP[W(CO)_5(CHDCHDPh)]$ (**4a**) has allowed for the first time a direct comparison of the stereochemistry of carboxylation and carbonylation processes (eq 1 and 2) involving the same metal-carbon center. Reaction 7, carbonylation of **4a**, proceeds smoothly with retention of configuration at the α -carbon atom, an observation consistent with all other stereochemically defined carbonylation processes.⁸



The retention of configuration at the originally metal-bound carbon atom of the phenethyl unit in the carboxylation and carbonylation reactions is indicative of a gross similarity in reaction pathways for these two processes. Hence, both CO_2 and CO insertion differ significantly from the sulfur dioxide insertion reaction which proceeds with inversion of configuration at the α -carbon center.^{3b,4} This stereochemical observation, coupled with detailed rate studies,⁹ indicates that the CO_2 -insertion reaction, like the corresponding process involving CO ,^{1,2} should be formulated as a *concerted* reaction. The transition state A for this process results from an attack of the nucleophilic $W(CO)_4[L]R^-$ ion at the electrophilic carbon or carbon oxygen center of CO_2 . The formation of a σ - $W-O$ bond and the simultaneous cleavage of the $W-C$ linkage leads to the carboxylate complex.¹⁶

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Formulation (8) is consistent with extensive kinetic measurements carried out on the CO₂ insertion reaction involving W(CO)₅Me⁻ as the substrate molecule.⁹ Positively charged interacting counterions are able to reduce the negative charge at the oxygen atom of the incipient carboxylate ligand and thereby accelerate the rate considerably, as studies in the presence of alkali ions have demonstrated.¹⁷ The participation of a free coordination site in the CO₂ insertion process is excluded by the fact that the CO₂ incorporation rate is not retarded in the presence of CO.⁹ Finally, the activation parameters for the CO₂ insertion process ($\Delta H^* = 42.7 \text{ kJ mol}^{-1}$ and $\Delta S^* = -181.2 \text{ J mol}^{-1}$, determined for PNP[*cis*-CH₃W(CO)₄P(OMe)₃] in THF)^{9,13} are consistent with a concerted (*I_a*) mechanism.

Relevant to the CO insertion reaction reported upon herein (eq 7), it is sufficient to reiterate that the stereochemical course observed for this process is in keeping with the well-accepted mechanism for this important class of organometallic reactions.^{4,5} The similarity of both the carboxylation and carbonylation is also demonstrated in the same rate dependence on the nature of the R group in W(CO)₅R⁻ moieties for the two insertion processes, i.e., R = Me > Ph. However, this dependence on R is much more dramatic for the carbonylation reaction.⁹

Spectroscopic Data of the Alkyl, Carboxylate-Tungsten Species 3a,b, 4a,b, 8a,b, 9, and 12a,b and the Phenylpropionyl-Tungsten Complex 13. The ¹H NMR signals of the α,β -dideuteriophenethyl ligand in **4a,b** appear as broadened doublets at 3.05 and 2.87 ppm, respectively, for the β -location and at 0.95 and 0.71 ppm, respectively, for the tungsten-bound CHD unit. In the case of **4b**, the latter resonance is further split into a doublet due to ³J_{H_WP} = 2.4 Hz. The α -CHD fragment resonances in the anionic complexes **4a,b** are shifted to higher field by 0.76 and 1.00 ppm, respectively, relative to the corresponding signals in the neutral *threo*-Cp(CO)₃WCHDCHDPh derivative.^{3b} In the spectra of the complexes **8a,b**, the two CHD units appear as quartets of the AB type at 2.90 and 2.43 ppm. The ³J_{H_{CH}} is found in all cases smaller than 7 Hz, demonstrating that **4a,b** and **8a,b** are three diastereomers.^{5d,8b,c,18} The corresponding signals of the unlabeled compounds **9** and **12a,b** are observed as complex AA'XX' and AA'BB', multiplets at the same chemical shifts. The phenylpropionyl complex **13** also has a *threo* configuration as indicated by ³J_{H_{CH}} = 4.3 Hz.^{5d,8b,c,18}

The infrared spectra of the pentacarbonyl species **3a, 4a, 8a, 9, 12a**, and **13** show in the carbonyl region the A₁^(1,2) and E vibrations typical for C_{4v} symmetry. The four ν (CO) absorptions noted for **3b, 4b, 8b**, and **12b** are consistent with a C_{2v} symmetry for the tungsten-tetracarbonyl fragment and therefore a *cis* coordination for the phenethyl or phenylpropionylate ligand, respectively, and the phosphine substituent. According to the higher density of charge at the metal center, the bands of the alkyl species appear at lower energy (10–35 cm⁻¹) than those of the CO₂ and

CO insertion products. All infrared data in the ν (CO) region are consistent with similarly obtained data for the analogous methyl-tungsten complexes.^{9,13,19}

In general, all spectra except those of **13** contained impurities due to the high instability of the synthesized compounds in solution; nevertheless, the absorptions could be located clearly by comparison with those of known samples of labeled and unlabeled complexes.

Experimental Section

All manipulations were carried out either in an argon drybox or on a double-manifold Schlenk vacuum line, using freshly distilled solvents. Reagent-grade tetrahydrofuran and hexane were purified by distillation under nitrogen from sodium benzophenone ketyl. Me₃P and [PNP][Cl] were purchased from Strem Chemicals, Inc. (Newburyport, MA 01950). Na[Naph],²⁰ PhCH₂CH₂OTs,⁹ *erythro*-PhCHDCHDOTs,^{8c} PNP[OTs],⁹ Na₂[W(CO)₄(L)] (L = CO and Me₃P),^{13,21} and PNP[W(CO)₅Cl]¹⁵ were prepared by the methods previously described. Proton NMR spectra were recorded on a Varian EM-390 spectrometer. Infrared spectra were recorded on either a perkin-Elmer 283B or an IBM FTIR/85 spectrometer.

Bis(triphenylphosphine)iminium *threo*-Pentacarbonyl(1,2-dideuterio-2-phenylethyl)tungstenate(0) (4a). To a freshly prepared solution of **1a** (0.3819 g, 1.0326 mmol) in 40 mL of THF a solution of **2** (0.3161 g, 1.1358 mmol) in 5 mL of THF was added dropwise at -78 °C. The reaction mixture changed color immediately from bluish green to yellow-brown; IR monitoring after addition of **2** proved complete formation of **3a**. After the solution was warmed to -20 °C, PNP[OTs] (0.9511 g, 1.3399 mmol) was added and the mixture was rapidly stirred for another hour at ambient temperature. Na[OTs] and excess PNP[OTs] were removed by centrifuging, and following filtration through Celite, the yellow-brown clear solution was evaporated in vacuo. The resulting brown oil was redissolved several times in 10 mL of THF and precipitated with 60 mL of hexane, followed by washing with ether and hexane. Drying in vacuo afforded 0.7610 g of yellow, powdery **4a** together with a small quantity of **5**.¹⁰ **3a**: IR (THF) ν (CO) 2022 (w), 1883 (s), 1839 (m), cm⁻¹. **4a**: ¹H NMR (THF-*d*₆) δ 7.40 (m, 35 H, PNP, Ph), 3.05 (d, ³J_{H_{CH}} = 3.6 Hz, 1 H, HDC-Ph), 0.95 (d, ³J_{H_{CH}} = 3.6 Hz, 1 H, HDC-W); IR (THF) ν (CO) 2028 (w), 1883 (s), 1839 (m) cm⁻¹.

Bis(triphenylphosphine)iminium *threo*-Tetracarbonyl(1,2-dideuterio-2-phenylethyl)(trimethylphosphine)tungstenate(0) (4b). In an analogous manner to that described for **4a**, **4b** was prepared from **1b** (0.4288 g, 1.0259 mmol), **2** (0.3141 g, 1.1285 mmol), and PNP[OTs] (0.8811 g, 1.2414 mmol). **6**¹¹ (0.1490 g) (32%) was separated from 0.3497 g (34%) of **4b** by reprecipitating the resulting oil 4 times from THF/hexane (1:3). **3b**: IR (THF) ν (CO) 1971 (w), 1855 (s), 1788 (m) cm⁻¹. **4b**: ¹H NMR (THF-*d*₆) δ 7.45 (m, 35 H, PNP, Ph), 2.87 (d, ³J_{H_{CH}} = 6.0 Hz, 1 H, HDC-Ph), 1.58 (d, ²J_{H_{CP}} = 6.6 Hz, 9 H, H₃CP), 0.71 (dd, ³J_{H_{CH}} = 6.0, ³J_{H_{CM}P} = 2.4 Hz, 1 H, HDC-W); IR (THF) ν (CO) 1969 (m), 1840 (s, br), 1785 (m) cm⁻¹.

Bis(triphenylphosphine)iminium *threo*-Pentacarbonyl(2,3-dideuterio-3-phenylpropionylato)tungstenate(0) (8a). A solution of **4a** (0.4000 g, 0.4125 mmol) in 80 mL of THF was pressurized with 400 psi CO₂ and rapidly stirred at ambient temperature in a 300 mL stainless steel Parr reactor. The reaction was monitored by infrared spectroscopy in the ν (CO) region. After 170 h, the reactor was depressurized and the reaction mixture filtered through Celite and evaporated in vacuo. The residue was purified from trace impurities of W(CO)₆ by several ether and hexane washings. It was not possible to separate **5** and **8a** after several reprecipitations from THF/hexane: total yield of **5** and **8a**, 0.2741 g. **8a**: ¹H NMR (THF-*d*₆) δ 7.50 (m, 35 H, PNP, Ph), 2.90, 2.43 (AB, ³J_{H_{CH}} = 5.1 Hz, 1 H, 1 H, HDC, HDC); IR (THF) ν (CO) 2058 (w), 1911 (vs), 1850 (m) cm⁻¹.

Bis(triphenylphosphine)iminium *threo*-Tetracarbonyl(2,3-dideuterio-3-phenylpropionylato)(trimethylphosphine)tungstenate(0) (8b). This complex was prepared by using the procedure outlined for the synthesis of **8a**, employing 0.4710 g (0.4628 mmol) of **4b**. The reaction time was approximately 80 min, and the product **8b** was separated from the impurity **6** (0.0845 g (41%)) by three precipitations from THF/hexane. Complete purification of **8b** was not possible because of its fast decomposition in solution to **6**. The yield of **8b** was 0.1243 g: ¹H NMR (THF-*d*₆) δ 7.50 (m, 35 H, PNP, Ph), 2.95, 2.50 (AB, ³J_{H_{CH}} = 5.7 Hz, 1 H, 1 H, HDC, HDC), 1.52 (d, ²J_{H_{CP}} = 7.1 Hz, 9 H, H₃CP); IR (THF)

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$\nu(\text{CO})$ 1995 (w), 1872 (vs), 1851 (s), 1797 (s) cm^{-1} .

Bis(triphenylphosphine)iminium Pentacarbonyl(2-phenylethyl)tungstenate(0) (9). Analogous to the preparation of **4a**, this derivative was obtained from **1a** (0.9542 g, 2.5797 mmol), $\text{PhCH}_2\text{CH}_2\text{OTs}$ (0.7841 g, 2.8377 mmol), and $[\text{PNP}][\text{Cl}]$ (1.6290 g, 2.8377 mmol): yield (with some impurities of **5**), 1.7973 g; $^1\text{H NMR}$ ($\text{THF}-d_6$) δ 7.40 (m, 35 H, PNP, Ph), 3.05, 0.95 (AA'XX', 2 H, 2 H, $\text{H}_2\text{C}-\text{Ph}$ and H_2CW , respectively). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF}/\text{THF}-d_6$) δ 208.1 (s, $^1J_{\text{CW}} = 146.2$ Hz, *trans*-CO), 207.4 (s, $^1J_{\text{CW}} = 126.2$ Hz, *cis*-CO), 153.2-123.2 (m, PNP, Ph), 47.1 (s, CH_2-Ph), -2.5 (s, $^1J_{\text{CW}} = 48.2$ Hz, CH_2-W); IR (THF) $\nu(\text{CO})$ 2028 (w), 1883 (s), 1839 (m) cm^{-1} .

Silver 3-Phenylpropionate (10a). To $\text{PhCH}_2\text{CH}_2\text{CO}_2\text{H}$ (3.0024 g, 19.976 mmol), suspended in 50 mL of H_2O , KOH (1.1208 g, 19.976 mmol) dissolved in 12 mL of H_2O was added. To the resulting clear solution of $\text{K}[\text{O}_2\text{CCH}_2\text{CH}_2\text{Ph}] \text{AgNO}_3$ (3.3902 g, 19.976 mmol) dissolved in 4 mL of H_2O was added dropwise with stirring. After 15 min, the white precipitate which formed was separated and washed 3 times with 10 mL of H_2O , 10 mL of MeOH, and 10 mL of ether followed by drying in vacuo over P_2O_5 : yield, 4.7239 g (92%); mp 269-271 °C dec.

Silver *threo*-2,3-Dideuterio-3-phenylpropionate (10b). This salt was prepared in a completely analogous manner as **10a** from 1.740 g (17.889 mmol) of *threo*- $\text{PhCHDCHDCO}_2\text{H}$,^{8b} 1.0037 g (17.889 mmol) of KOH, and 3.0388 g (17.889 mmol) of AgNO_3 : yield, 4.2169 g (91%); mp 261-264 °C dec.

Bis(triphenylphosphine)iminium Pentacarbonyl(3-phenylpropionylato)tungstenate(0) (12a). A mixture of **10a** (0.2571 g, 1.0004 mmol) and **11** (0.6910 g, 0.7695 mmol) in 30 mL of THF was stirred for 80 min in the dark. The precipitate of AgCl and excess **10a** (0.1683 g) was separated by centrifuging. The clear, yellow solution of **12a** was evaporated in vacuo. Redissolving the remaining oil in 15 mL of THF, adding 30 mL of hexane, and washing the separated oil 4 times with 10 mL of hexane, followed by drying in vacuo afforded 0.6120 g (78%) of yellow, microcrystalline **12a**: $^1\text{H NMR}$ ($\text{THF}-d_6$) δ 7.50 (35 H, PNP, Ph), 2.90, 2.43 (AA'BB', 2 H, 2 H, $\text{H}_2\text{C}-\text{Ph}$ and $\text{H}_2\text{C}-\text{CO}_2$, respectively). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF}/\text{THF}-d_6$) δ 205.4 (s, $^1J_{\text{CW}} = 159.2$ Hz, *trans*-CO), 201.2 (s, $^1J_{\text{CW}} = 132.1$ Hz, *cis*-CO), 176.3 (s, OC(O)), 143.9-125.0 (m, PNP, Ph), 38.6, 33.4 (s, s, CH_2 , CH_2); IR (THF) $\nu(\text{CO})$ 2058 (w), 1911 (vs), 1850 (m) cm^{-1} .

Bis(triphenylphosphine)iminium *threo*-Pentacarbonyl(2,3-dideuterio-

3-phenylpropionylato)tungstenate(0) (8a). This derivative was obtained by the methodology of **12a** from 0.7215 g (0.8035 mmol) of **11** and 0.2617 g (1.0043 mmol) of **10b**: yield, 0.7412 g (91%).

Bis(triphenylphosphine)iminium Tetracarbonyl(trimethylphosphine)-(3-phenylpropionylato)tungstenate(0) (12b). A solution of **12a** (0.6940 g, 0.6860 mmol) and Me_3P (0.1044 g, 1.3720 mmol) in 25 mL of THF was heated to 50 °C for 40 min. The clear yellow solution was then evaporated in vacuo to a yellow oil, which was redissolved in 10 mL of THF. Addition of 30 mL of hexane led to the separation of 0.5234 g (72%) of yellow, powdery **12b** from 0.0362 g (12%) of **6**. **12b**: $^1\text{H NMR}$ ($\text{THF}-d_6$) δ 7.50 (m, 35 H, PNP, Ph), 2.95, 2.50 (AA'BB', 2 H, 2 H, H_2CPh and H_2CCO_2 , respectively), 1.52 (d, $^2J_{\text{HCP}} = 7.1$ Hz, 9 H, H_3CP); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF}/\text{THF}-d_6$) δ 213.1 (d, $^2J_{\text{CWP}} = 38.5$ Hz CO_{eq} , *trans* to Me_3P), 212.5 (d, $^2J_{\text{CWP}} = 8.3$ Hz, CO_{eq} *cis* to Me_3P), 206.8 (d, $^2J_{\text{CWP}} = 8.3$ Hz, CO_{ax}), 176.0 (d, $^3J_{\text{COWP}} = 1.8$ Hz, OC(O)), 144.2-124.9 (m, PNP, Ph), 39.2, 33.4 (s, s, CH_2 , CH_2), 18.17 (d, $^2J_{\text{CHP}} = 21.9$ Hz, CH_3P). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{THF}/\text{THF}-d_6$) δ 227.4 (s, $^1J_{\text{PW}} = 224.2$ Hz, PW), 25.86 (s, PNP); IR (THF) $\nu(\text{CO})$ 1995 (w), 1872 (vs), 1851 (s), 1797 (s) cm^{-1} .

Bis(triphenylphosphine)iminium *threo*-Tetracarbonyl(2,3-dideuterio-3-phenylpropionylato)(trimethylphosphine)tungstenate(0) (8b). This complex was prepared in an analogous manner to **12b** from 0.6040 g (0.5959 mmol) of **8a** and 0.0907 g (1.1917 mmol) of Me_3P : yield, 0.5314 g (84%).

Bis(triphenylphosphine)iminium Pentacarbonyl(3-phenyl-2,3-dideuterio-3-phenylpropionylato)tungstenate(0) (13). A solution of **4a** (0.4410 g, 0.4548 mmol) in 50 mL of THF was pressurized with 400 psi of CO at 25 °C in a stainless steel Parr reactor. After 2.5 h of rapid stirring, the reaction mixture was brought to atmospheric pressure and the yellow solution was evaporated to a yellow oil. Recrystallization from THF/toluene at -10 °C provided 0.3981 g (88%) of yellow crystalline **13**: $^1\text{H NMR}$ ($\text{THF}-d_6$) δ 7.55 (m, 35 H, PNP, Ph), 2.98, 2.80 (AB, $^3J_{\text{HCCH}} = 4.3$ Hz, 1 H, 1 H, HDC, HDC); IR (THF) $\nu(\text{CO})$ 2039 (w), 1895 (vs), 1864 (m), $\nu\text{C(O)}$ 1558 (w) cm^{-1} .

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Convergent Functional Groups: Synthetic and Structural Studies

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Abstract: The synthesis of new molecular systems in which carboxyl groups are directed at well-defined microenvironments is described. The structures are obtained by condensation of suitable aromatic diamines with triacid **4a**. Crystallographic studies establish the structural details of the systems and lead to the design and preparation of systems featuring a molecular cleft. These new molecules resemble enzymes in which carboxyl groups converge at the active sites.

It was on account of our foundering in olefin epoxidation¹ that we became involved with molecules in which carboxyl groups are imbedded in rigid, well-defined microenvironments. The intent was to exploit the high selectivity anticipated for reactions of such systems, as is the case when the carboxyl function is found in enzyme interiors. After considerable screening we have devised a new molecular scaffold on which carboxyl groups are arranged in the desired sense. Here we report the development and characterization of these systems; in the sequel, their binding properties as molecular receptors and their application to the Prilashajew reaction are described.

Stereoelectronics

The specific issue concerns the trajectory, i.e., the stereoelectronics of reactions involving carboxyl oxygen. Unlike carbonyl carbon, which enjoys ample attention in acyl transfer and aldol reactions, the carboxyl oxygen has been ignored as a relatively colorless entity, about which little could be done, anyway. An exception to this ignorance is the thoughtful analysis provided by Gandour² on the subject of general base catalysis by carboxylate. While his cases involve proton transfers, the conclusions, summarized in eq 1, are relevant to the reactions of carboxylate with electrophiles in general. Gandour points out that proton transfers

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(2) Gandour, R. *Bioorg. Chem.* 1981, 10, 169-176.