

the 12 valine spin systems in apoNCS were identified by using RELAY, and the 6 leucines were identified by using MLEV-16. If only the MLEV-16 experiment were performed, it could be difficult to discriminate between the valine C^αH-C^γH₃ and leucine C^αH-C^βH₃ cross peaks, although the latter are usually (but not always) weaker. Performing both experiments usually overcomes the ambiguity.

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Registry No. Neocarzinostatin, 9014-02-2.

Incorporating CO into Poly(alkoxymethylene)acyl Ligands. Converting (Ph₂PCH₂CH₂PPh₂)(CO)₂Co-COCH₃ into *threo*-(dppe)(CO)₂Co-COCH(OEt)CH(OEt)CH₃

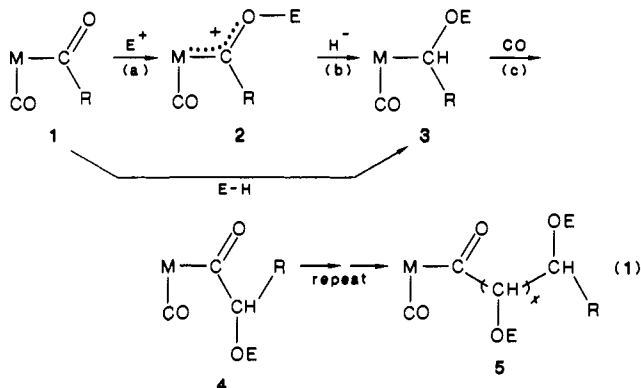
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Small organic molecules (C₁-C₄) can be prepared from carbon monoxide with transition organometallic complexes as templates.^{1,2} As a result of these studies, converting CO into poly(alkoxymethylene)acyl ligands **5** that retain an oxygen functionality on each carbon center³ can be addressed. These acyl complexes could derive from repeating a three-step sequence of ligand reactions (eq 1): (a) electrophilic activation of an acyl ligand, (b) hydride



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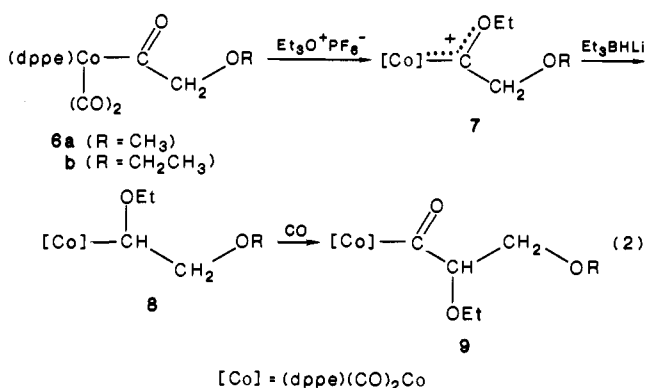
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(3) A limited number of complexes bearing such highly oxygenated alkyl ligands (having two or more alkoxy groups) have been reported.^{2a,3a-c} These include glycosylmetallate complexes (and their acyl derivatives) derived from *c*-glycoside halides.^{3d} (a) Rosenblum, M.; Turnbull, M. M.; Foxman, B. M. *Organometallics* **1986**, *5*, 1062. (b) Finke, R. G.; McKenna, W. P.; Schiraldi, D. A.; Smith, B. L.; Pierpont, C. J. *Am. Chem. Soc.* **1983**, *105*, 7592, 7605. (c) Schubert, U.; Fischer, E. O. *Justus Liebigs Ann. Chem.* **1975**, 393. Fischer, E. O.; Schubert, U.; Kalbfus, W.; Kreiter, C. G. *Z. Anorg. Allg. Chem.* **1975**, *416*, 135. Doetz, K. H.; Kuhn, W.; Thewalt, U. *Chem. Ber.* **1985**, *118*, 1126. (d) Rosenthal, A.; Koch, H. J. *Tetrahedron Lett.* **1967**, 871. DeShong, P.; Slough, G. A.; Elango, V.; Trainor, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 7788. Trainor, G. L.; Swart, B. E. *J. Org. Chem.* **1983**, *48*, 2447. Trainor, G. L. *J. Organomet. Chem.* **1985**, *282*, C43.

transfer to its oxycarbenoid derivative **2**, and (c) carbonylation of the resulting alkoxyalkyl group on **3**.⁴ The first two steps, net reduction of the acyl ligand, are well established for alkoxy carbene complexes (E = CH₃, CH₂CH₃).⁵ Carbonylating alkyl ligands bearing α -alkoxy substituents (step c), however, is relatively difficult⁶ and only occurs in more labile organometallic systems.⁷

We now report coupling the acyl reduction (a and b) and carbonylation (c) steps by using the (dppe)(CO)₂Co system (dppe = Ph₂PCH₂CH₂PPh₂).⁸ These reactions moreover are stereoselective: complete diastereofacial selectivity at each emerging chiral center (step b) is observed in forming the cobalt diethoxybutanoyl **5** (x = 1, E = Et, R = CH₃).

Cobalt-alkoxyacetyl complexes **6a,b** were converted to their dialkoxypropionyl derivatives **9b** (eq 2) (overall yields 63-72%).



The starting **6a,b** were obtained (72-76% yields) after carbonylating (1 atm, 8 h) THF solutions containing (dppe)(CO)₂Co-CH₂OR, which were generated by alkylating (dppe)(CO)₂Co-Na⁺ with chloromethyl ethers.⁹ Treating **6a,b** in CH₂Cl₂ successively with Et₃O⁺PF₆⁻, with LiHBEt₃ (-80 °C, 1 h), and with CO (1 atm at 22 °C, 10 h) affords **9a,b**. These result as air-stable, yellow crystals after combined column chromatography (alumina-CH₂Cl₂) and crystallization from CH₂Cl₂-ether-pentane. All acyl complexes reported herein are characterized by IR and ¹H, ¹³C, and ³¹P NMR spectroscopy and by acceptable elemental microanalyses.¹⁰

(4) In related studies, B₂H₆ or BH₃·THF have been used in incorporating CO into methyl complexes to give acyl derivatives M-CO(CH₂)_xCH₃ (x = 0-3). Chain growth entails BH₃ reduction of an acyl to its homologous saturated alkyl ligand, which then inserts CO. Stimson, R. E.; Shriver, D. F. *Organometallics* **1982**, *1*, 787. Brown, S. L.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1986**, 84.

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(9) Experimental procedures resemble those used in preparing (PMePh₂)₂(CO)₂ cobalt-alkyl and -acyl complexes.^{7d}

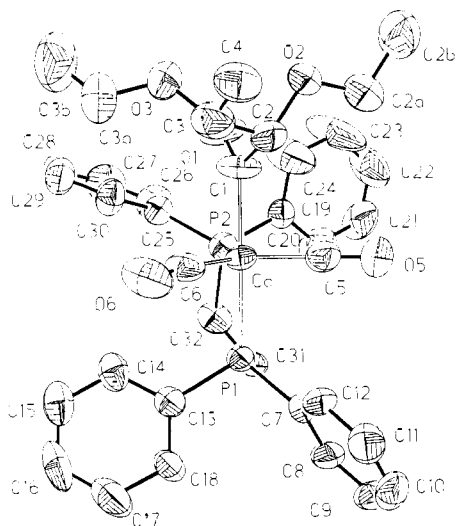
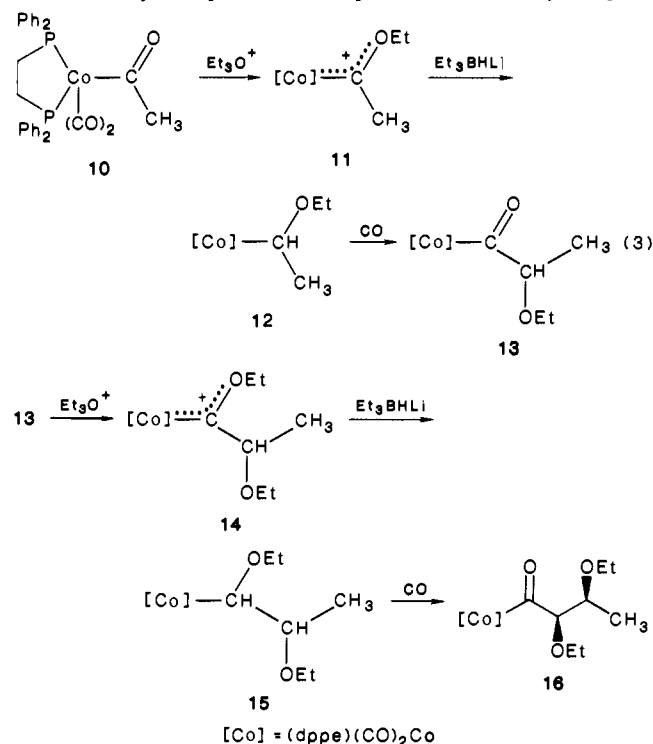


Figure 1. ORTEP plot of **16** with 50% probability thermal ellipsoids (hydrogen atoms omitted). Selected bond distances (Å) and angles (deg) are as follows: Co–C(1), 1.979 (7); C(1)–O(1), 1.181 (11); Co–P(2), 2.233 (2); Co–C(5), 1.764 (9); Co–C(6), 1.742 (9); Co–P(1), 2.240 (2); C(1)–Co–P(1), 177.1 (3); P(1)–Co–P(2), 86.2 (1); C(5)–Co–C(6), 125.6 (4); C(1)–Co–C(5), 89.2 (4); C(6)–Co–P(2), 127.6 (3).

The same sequence of ligand reactions repeated twice starting with the acetyl complex **10**^{8b} incorporates two carbonyls (eq 3).



Thus, **10** successively gives the ethoxypropionyl complex **11** (yellow crystals, 81% yield) and then its diethoxybutanoyl homolog **16**¹⁰ (74% yield from **10**).¹² Only one diastereomer of **16** is detected,

(10) See Supplementary Material. The corresponding η^1 -alkyl and alkoxy-carbene complexes are much less stable and were only spectroscopically characterized. Although isolated as yellow-brown solids, (dppe)(CO)₂Co-alkyl and -alkoxy-carbene complexes slowly decompose upon attempted storage of solids (–20 °C) or in CH₂Cl₂ or benzene solution. IR and ³¹P NMR spectroscopies are sensitive spectral probes for monitoring the coordinated ligand reactions: cobalt-acyl complexes, $\nu(\text{CO})$ 1980, 1920 cm^{–1} [acyl $\nu(\text{C}=\text{O})$ 1630 cm^{–1}] and δ 66; cobalt-alkoxy-carbene, $\nu(\text{CO})$ 2025, 1975 cm^{–1} and δ 74; cobalt-alkoxyalkyl, $\nu(\text{CO})$ 1968, 1910 cm^{–1} and δ 71. Broad singlets observed by ³¹P NMR spectroscopy (+30 °C) afford two doublets ($J = 23$ Hz) when the data is taken at lower temperatures (<–30 °C). At these temperatures, the presumed Berry pseudorotation (which interconverts the nonequivalent dppe phosphine centers) is frozen.¹¹

however, and this is assigned as the threo or syn configuration¹³ on the basis of its ¹H NMR spectrum (vicinal $J_{\text{HH}} = 5.7$ Hz)¹⁴ and its single-crystal X-ray structure determination.¹⁵

In the solid state, **16** adopts a trigonal bipyramidal structure (Figure 1) having two equatorial carbonyls, an axial acyl ligand, and the dppe chelate spanning axial-equatorial positions. The threo configuration of the acyl group also is evident (only one enantiomer is illustrated), and the puckered dppe chelate, as expected,¹⁶ presents an alternating “edge-face” array of phenyl rings.¹⁶ Phenyl rings on the equatorial phosphine P(2) evidently do not shield the proximate face of the acyl carbonyl, C(1)–C(19) = 3.68 Å and C(1)–C(25) = 3.73 Å, as has been suggested for PPh₃-containing pseudooctahedral iron acyl complexes.¹⁷ The high diastereofacial selectivity observed in reducing **14**, however, is consistent with a Felkin-Anh transition-state argument: 1,2-asymmetric induction originates in the hydride delivery anti-periplanar to the β -ethoxy group.¹⁸ Studies in progress will test this stereochemistry model in terms of incorporating CO into a growing metal-bound poly(alkoxymethylene) chain.

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Supplementary Material Available: Tables I–IX (infrared spectral and microanalytical data for acyl complexes, NMR spectral data for (dppe)(CO)₂Co-acyl complexes, spectral data for (dppe)(CO)₂Co-acyl and -carbene complexes, crystal data, atomic coordinates and isotropic thermal parameters, bond lengths,

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(12) (dppe)(CO)₂Co–CO–CH(OEt)CH(OEt)CH₃ (**16**): mp 147–148 °C; IR (CH₂Cl₂) 1978, 1919 cm^{–1} (C=O), 1632 cm^{–1} (C=O); ¹H NMR (200 MHz, C₆D₆) δ 4.20 (quint, $J = 6.0$ Hz, CoCOCHCH), 3.97 (d, $J = 5.7$ Hz, CoCOCHCH), 3.64 (dq, $J = 7.0, 8.9$ Hz, CoCOCHCHCHCH₃), 3.42 (dq, $J = 7.0, 8.9$ Hz, CoCOCHCHCHCH₃), 3.52 (dq, $J = 7.0, 9.2$ Hz, CoCOCHCHCHCHCH₃), 3.49 (dq, $J = 7.0, 9.2$ Hz, CoCOCHCHCHCHCH₃), 1.21 (t, $J = 7.0$ Hz, CoCOCHCHCH₃), 1.16 (d, $J = 6.4$ Hz, CoCOCHCHCH₃), 1.12 (t, $J = 7.0$ Hz, CoCOCHCH(OCH₂CH₃)); ¹³C{¹H} NMR (C₆D₆) δ 250.2 (t, $J = 13$ Hz, CoCOCH), 204.9 (br s, CO) 99.8 (t, $J = 11$ Hz, CoCOCH), 74.6 (CoCOCHCH), 66.6 (CoCOCH(OCH₂CH₃)), 64.3 (CoCOCHCH(OCH₂CH₃)), 16.6 (CoCOCHCHCH₃), 15.5, 15.4 (CoCOCH(OCH₂CH₃)CH(OCH₂CH₃)); ³¹P{¹H} NMR (PhCH₃) δ 66.1. Anal. Calcd for C₃₆H₃₉CoO₅P₂: C, 64.24; H, 5.80. Found: C, 64.11; H, 5.72.

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(15) Crystal data: (Ph₂PCH₂CH₂PPh₂)(CO)₂CoCOCH(OCH₂CH₃)CH(OCH₂CH₃)CH₃ (**16**) as yellow crystals by slow diffusion of pentane into a CH₂Cl₂ solution; 0.16 × 0.22 × 0.36 mm, P2₁/n (no. 14), $a = 11.010$ (3) Å, $b = 18.709$ (6) Å, $c = 16.473$ (6) Å, $\beta = 92.88$ (2)°, $V = 3389.0$ (16) Å³, $Z = 4$, $\rho(\text{calcd}) = 1.32$ g/cm³. Nicolet R3M diffractometer, $\mu = 6.6$ cm^{–1} (Mo K α) (empirical absorption correction applied), 22 °C, $2\theta_{\text{max}} = 48^\circ$, $N_{\text{refl}} = 6241$, ($I > 3\sigma_I$) = 3226. $R = 0.0762$, $R_w = 0.0721$. Heavy-atom solution, blocked cascade refinement, all non-hydrogen atoms anisotropic, all hydrogen atoms as idealized, isotropic contributions. SHELXTL (revision 5.1) computer programs (Nicolet Corp., Madison, WI).

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bond angles, anisotropic thermal parameters, and H-atom coordinates and isotropic thermal parameters) and Figures 2–6 (^1H NMR spectrum of **16**, three ORTEP plots of **16**, and a diagram from atomic coordinates) (22 pages). Ordering information is given on any current masthead page.

Identification of Intermediates and Products in the Reaction of Porphyrin Iron(III) Alkyl Complexes with Dioxygen

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Unlike most $\text{PFe}^{\text{III}}+$ (P is a porphyrin dianion) complexes, complexes of the type $\text{PFe}^{\text{III}}\text{CH}_2\text{R}$ (R = H or CH_3) are reactive toward dioxygen with the ubiquitous $\text{PFe}^{\text{III}}\text{O}-\text{Fe}^{\text{III}}\text{P}$ as the only reported product.¹ Here we report on ^1H NMR studies of this reaction which focus on the detection of intermediates and the fate of the alkyl group. These results should be viewed in the context of extensive previous studies on model systems for dioxygen activation in biological systems (heme oxygenases) involving reaction of dioxygen with PFe^{II} and on the interaction of peracids and hydroperoxides with PFe^{III} .² Through these studies a number of reactive intermediates including the peroxo-bridge complex, $\text{PFe}^{\text{III}}\text{O}-\text{O}-\text{Fe}^{\text{III}}\text{P}$, and the ferryl complexes, $\text{PFe}^{\text{IV}}=\text{O}$, (B) $\text{P}-\text{Fe}^{\text{IV}}=\text{O}$ (B is an amine), and (P*) $\text{Fe}^{\text{IV}}=\text{O}^+$ (P* is a porphyrin radical monoanion), have been detected.

Exposure of a toluene solution of $\text{TTPFe}^{\text{III}}\text{CH}_3$ (TTP is the dianion of tetra(*p*-tolyl)porphyrin) to dioxygen at -80°C produces the ^1H NMR spectrum shown at the top of Figure 1. Three species, unreacted $\text{TTPFe}^{\text{III}}\text{CH}_3$, A, and two intermediates, B and C, are present. The distinctive resonance patterns for B and C are consistent with their formulation as high-spin ($S = 5/2$), five-coordinate iron(III) complexes.⁴ The line widths of the pyrrole resonances (B, 1490 Hz; C, 1170 Hz) are consistent with an oxygen donor occupying the fifth coordination site.⁵ Intermediate B is quite unstable, even at -80°C . After standing for

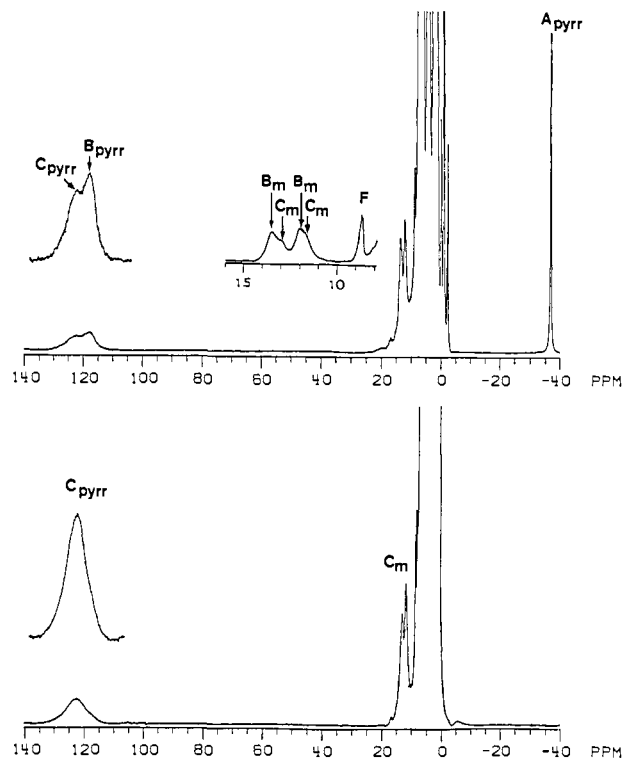


Figure 1. The 360-MHz ^1H NMR spectrum of a toluene- d_8 solution of $\text{TTPFe}^{\text{III}}\text{CH}_3$ at -80°C (a) after the addition of (b) 2 h later. Peaks due to $\text{TTPFe}^{\text{III}}\text{CH}_3$ and the two intermediates are labeled A, B, and C, respectively. Formaldehyde is labeled F, but its intensity is not comparable to other paramagnetic peaks because of spectrometer conditions. The pyrrole resonances are indicated by subscript pyrr, and the meta/phenyl resonances by subscript m.

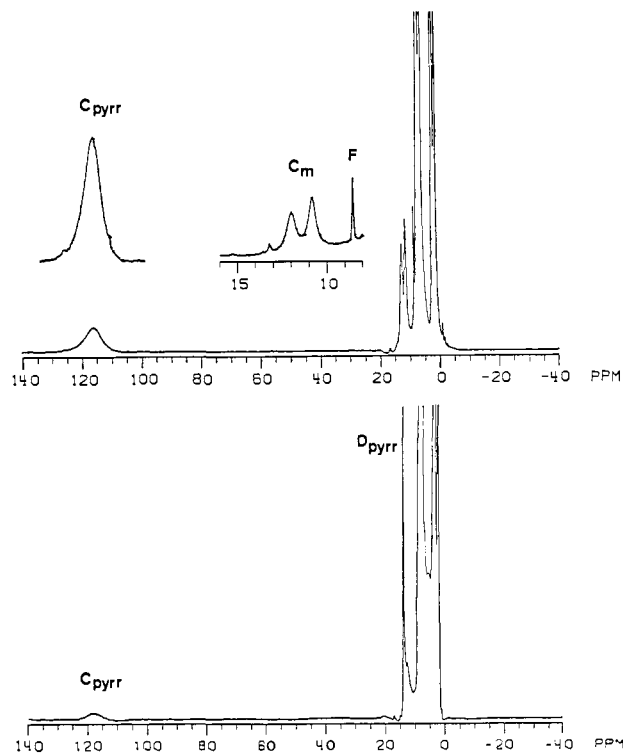


Figure 2. The 360-MHz ^1H NMR spectrum of the sample shown in Figure 1: (a) after warming to -70°C and (b) after warming to 25°C , storing for 2 h at 25°C , and then cooling back to -70°C . Peaks are labeled as in Figure 1 with D indicating $\text{TTPFe}^{\text{III}}\text{OFe}^{\text{III}}\text{TTP}$.

2 h at -80°C , the ^1H NMR spectrum of the sample is converted into that shown in the lower trace of Figure 1. Only C is present.

Intermediate C is also unstable. Figure 2 shows the ^1H NMR

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