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Manganese-centered coupling of pentadienyl ligands. Isolation of a metal complex of the coupled product

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correct, small quantities of an added Lewis acid, say BBr_3, should catalyze the reaction by trapping the free Me_2S. In fact, 5 mol % of BBr_3 catalyzes the hydroboration of 1-hexene with $BHBr_2{\cdot}SMe_2$ remarkably (Table I).

The dissociation mechanism (eq 2–4) clearly explains why $BHBr_2{\cdot}SMe_2$ is able to hydroborate alkenes much faster than $BHCl_2{\cdot}SMe_2$. $RBCl_2{\cdot}SMe_2$ is a weaker complex than $RBBr_2{\cdot}SMe_2$ since $RBCl_2$ is a weaker Lewis acid than $RBBr_2$. As a result, $RBCl_2{\cdot}SMe_2$ dissociates into $RBCl_2$ and Me_2S to a greater extent than does $RBBr_2{\cdot}SMe_2$ and thus has a larger rate-retarding effect on the reaction with the alkene.

We now have a general understanding on the mechanism of hydroboration of alkenes by borane·Lewis base adducts. The evidence presented in this paper on the behavior of $BHBr_2{\cdot}SMe_2$ reinforces superbly our conclusions on 9-BBN·Lewis base adducts. Pasto and co-workers examined the reaction of 2,3-dimethyl-2-butene with $H_2BCl{\cdot}THF$ in THF[14] as well as the reaction of the same alkene with $BH_3{\cdot}THF$.[15] Both reactions displayed second-order kinetics, first-order in 2,3-dimethyl-2-butene and first-order in borane complex. From the observed entropies of activation, they deduced that the reactions must proceed through a direct reaction of the alkene with the borane complex. Our observations on the 9-BBN·Lewis base adducts and $BHBr_2{\cdot}SMe_2$ argue strongly for the dissociation mechanism.

The catalysis of the hydroboration of alkenes by small quantities of BBr_3 is of immediate use in organic synthesis. Even though $BHBr_2{\cdot}SMe_2$ is capable of hydroborating many alkenes at satisfactory rates even in the absence of added Lewis acid, with less reactive alkenes such as cyclohexene, the reaction is very slow and it is practically impossible to complete the reaction.[16] With 10 mol % of BBr_3 as the catalyst, we are able to effect the hydroboration of cyclohexene to completion in 6 h in CH_2Cl_2 at reflux temperature (Table I).

In conclusion, the identification of the correct mechanism of hydroboration by $BHBr_2{\cdot}SMe_2$ has resulted in the discovery of a remarkable catalysis by small quantities of BBr_3.

Acknowledgment. We gratefully acknowledge the financial support (Grant CHE 79-18881) from the National Science Foundation. We thank Professor Kung K. Wang for helpful discussions.

Registry No. (*n*-hexyl)$BBr_2{\cdot}SMe_2$, 64770-04-3; $BHBr_2{\cdot}SMe_2$, 55671-55-1; BBr_3, 10294-33-4; cyclohexene, 110-83-8; 1-hexene, 592-41-6.

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[14] Pasto, D. J.; Kang, S.-Z. *J. Am. Chem. Soc.* **1968**, *90*, 3797–3800.

[15] Pasto, D. J.; Lepeska, B.; Cheng, T.-C. *J. Am. Chem. Soc.* **1972**, *94*, 6083–6090.

[16] We circumvented this problem earlier by doing the hydroboration of cyclohexene with $BHBr_2{\cdot}SMe_2$ in the presence of 1 molar equiv of BBr_3. Recently, (cyclohexyl)BBr_2 has been made conveniently by a redistribution of tricyclohexylborane with BBr_3 in the presence of BMS as the catalyst (Brown, H. C.; Basavaiah, D.; Bhat, N. G. *Organometallics*, in press).

Manganese-Centered Coupling of Pentadienyl Ligands. Isolation of a Metal Complex of the Coupled Product

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Summary: Reaction of $MnBr_2$ with potassium 2,4-dimethylpentadienide and $P(CH_3)_3$ results in the formation of (η^8-2,4,7,9-tetramethyl-1,3,7,9-decatetraene)(trimethylphosphine)manganese (**1**). *The decatetraene ligand is derived from the manganese-centered coupling of two 2,4-dimethylpentadienyl ligands.* The crystal structure of **1**, as determined by a single-crystal X-ray diffraction study, is reported. A mechanism for the pentadienyl coupling reaction is proposed.

Although cyclopentadienylmetal complexes are ubiquitous in organotransition-metal chemistry, the synthesis and reactivity of metal complexes possessing *acyclic* pentadienyl ligands remains largely unexplored.[1,2] Because the acyclic pentadienyl ligand can adopt a variety of bonding modes (η^5,[1,2] η^3,[3] and probably η^1), we anticipate that pentadienylmetal complexes will, in general, possess a rich reaction chemistry. We now report the phosphine-induced, manganese-centered coupling of two acyclic pentadienyl ligands and the isolation of a manganese–phosphine complex of the coupled product. The stereochemistry of the coupled product has led us to postulate a coupling mechanism involving bis(η^3-pentadienyl)manganese intermediates.

The reaction of $MnBr_2$ with potassium 2,4-dimethylpentadienide[4] and $P(CH_3)_3$ in tetrahydrofuran at −78 °C, followed by warming to room temperature with vigorous stirring, produced in high yield a green, paramagnetic, pentane-soluble complex, (η^8-2,4,7,9-tetramethyl-1,3,7,9-decatetraene)(trimethylphosphine)manganese (1).[5,6] A single-crystal X-ray diffraction study of 1 was carried out.[7] An ORTEP drawing of the molecular structure is shown in Figure 1, and selected bond lengths and angles are given in Table I. The molecular geometry is square pyramidal with the four C–C double bonds of the decatetraene ligand occupying basal sites and the phosphorus atom of the $P(CH_3)_3$ ligand occupying the axial site.[8] The two butadiene moieties of the decatetraene ligand are planar and are fully eclipsed. The two internal double bonds of the decatetraene ligand have trans configurations (vide infra). The methyl groups bonded to C4 and C7 are displaced substantially out of the plane of their respective butadiene fragments away from the manganese atom (C4′ is 1.217 Å from the plane containing C1, C2, C3, and C4, while C7′ is 1.234 Å from the plane containing C7, C8, C9, C10).[9] In

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[1] An important contribution to this area has recently been made by Ernst, who has synthesized a series of "open metallocenes", i.e., metallocene analogues possessing two η^5-acyclic pentadienyl ligands: Wilson, D. R.; DiLullo, A. A.; Ernst, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5930. Wilson, D. R.; Liu, J.-Z.; Ernst, R. D. Ibid. **1982**, *104*, 1120. Liu, J.-Z.; Ernst, R. D. Ibid. **1982**, *104*, 3737.

[2] Other reports of pentadienylmetal complexes include the following: (a) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 1511. (b) Giannini, U.; Pellino, E.; Lachi, M. P. *J. Organomet. Chem.* **1968**, *12*, 551. (c) Seyferth, D.; Goldman, E. W.; Pornet, J. *J. Organomet. Chem.* **1981**, *208*, 189. (d) Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1982**, *1*, 708.

[3] We have recently synthesized and carried out a single-crystal X-ray diffraction study on (η^3-2,4-dimethylpentadienyl)tris(trimethylphosphine)cobalt. The η^3-2,4-dimethylpentadienyl ligand in this complex adopts an anti (U-shaped) configuration: Bleeke, J. R.; Peng, W.-J., submitted for publication.

[4] Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036.

[5] In a typical reaction, 0.152 g (7.08×10^{-4} mol) of $MnBr_2$ was refluxed in tetrahydrofuran for 0.5 h. The solution was cooled to −78 °C, and 1.08 g (1.42×10^{-2} mol) of $P(CH_3)_3$ and 0.220 g (1.07×10^{-3} mol) of potassium 2,4-dimethylpentadienide–tetrahydrofuran ($KC_7H_{11}{\cdot}C_4H_8O$) in tetrahydrofuran were added slowly with stirring, producing an orange solution. This solution was allowed to warm to room temperature and stirred for 12 h. The resulting green solution was filtered through Celite and evaporated to dryness. The green product 1 was extracted with pentane and crystallized from pentane at −30 °C: yield (based on limiting reagent, $KC_7H_{11}{\cdot}C_4H_8O$) 0.15 g (87.2%). All manipulations were carried out under N_2.

[6] MS (chemical ionization, CH_4, 120 eV) M^+. Anal. Calcd for $MnPC_{17}H_{31}$: C, 63.53; H, 9.74. Found: C, 63.01; H, 9.52.

Table I. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (η^8-2,4,7,9-tetramethyl-1,3,7,9-decatetraene)(trimethylphosphine)manganese (1)

		Bond Distances			
Mn-P	2.290 (1)	P-C1P	1.824 (5)	C5-C6	1.436 (8)
Mn-C1	2.127 (4)	P-C2P	1.841 (4)	C6-C7	1.527 (6)
Mn-C2	2.122 (4)	P-C3P	1.833 (5)	C7-C8	1.430 (6)
Mn-C3	2.071 (4)	C1-C2	1.392 (6)	C7-C7′	1.512 (6)
Mn-C4	2.123 (4)	C2-C3	1.401 (6)	C8-C9	1.422 (5)
Mn-C7	2.140 (4)	C2-C2′	1.516 (5)	C9-C10	1.399 (6)
Mn-C8	2.053 (4)	C3-C4	1.438 (5)	C9-C9′	1.500 (6)
Mn-C9	2.118 (4)	C4-C5	1.524 (6)		
Mn-C10	2.132 (4)	C4-C4′	1.506 (6)		
		Bond Angles			
P-Mn-C1	88.2 (1)	C1-C2-C3	120.7 (4)	C5-C6-C7	116.8 (4)
P-Mn-C2	123.8 (1)	C1-C2-C2′	120.4 (4)	C6-C7-C8	114.8 (4)
P-Mn-C3	128.4 (1)	C3-C2-C2′	118.7 (4)	C6-C7-C7′	113.3 (4)
P-Mn-C4	93.9 (1)	C2-C3-C4	123.1 (4)	C8-C7-C7′	119.2 (4)
P-Mn-C7	91.0 (1)	C3-C4-C5	113.9 (4)	C7-C8-C9	122.2 (4)
P-Mn-C8	127.0 (1)	C3-C4-C4′	120.1 (4)	C8-C9-C10	119.0 (4)
P-Mn-C9	125.1 (1)	C5-C4-C4′	113.3 (4)	C8-C9-C9′	118.7 (4)
P-Mn-C10	89.7 (1)	C4-C5-C6	118.0 (4)	C10-C9-C9′	122.1 (4)

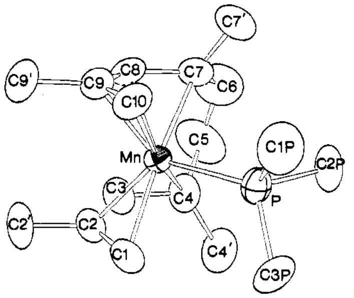
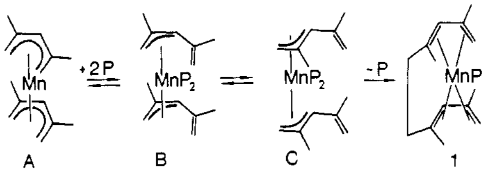


Figure 1. ORTEP drawing for (η^8-2,4,7,9-tetramethyl-1,3,7,9-decatetraene(trimethylphosphine)manganese (1). Atoms are represented by thermal vibration spheres drawn to encompass 50% of the electron density. All hydrogen atoms are omitted for clarity.

contrast, methyl carbon atoms C2′ and C9′ are essentially in the plane of their respective butadiene fragments. The C–C bond distances within the butadiene moieties vary from 1.392 (6) to 1.438 (5) Å. The C–C bond in the ethylene bridge *appears to be* anomalously short, 1.436 (8) Å, but this is probably an artifact of a minor disorder in the positions of C5 and C6.[10] Mn–C distances vary from 2.053 (4) to 2.140 (4) Å. The Mn–C3 and Mn–C5 bonds are significantly shorter than the other six Mn–C bonds.[11]

Scheme I



In Scheme I, we propose a mechanism for this pentadienyl coupling reaction, which accounts for the observed trans,trans stereochemistry of the decatetraene ligand. We suggest that "open manganocene", A, is formed at low temperature[12] but upon warming reacts with phosphine to produce the *anti*,*anti*-bis(η^3-pentadienyl)bis(trimethylphosphine)manganese intermediate B. This intermediate equilibrates with its syn,syn isomer C.[13]

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(7) Crystals (green plates) suitable for X-ray diffraction were obtained from a saturated hexane solution at −30 °C. The single crystals were monoclinic, space group $P2_1/c$ (No. 14) with $a = 8.017$ (2) Å, $b = 14.771$ (4) Å, and $c = 15.878$ (4) Å, $\beta = 113.32$ (3)°, and $Z = 4$. X-ray diffraction data were collected at room temperature on a Nicolet P3 diffractometer, using graphite-monochromated Mo Kα radiation. A total of 3425 independent reflections with $0° < 2\theta < 50°$ were collected, employing the θ–2θ scanning technique and a scan rate of 4°/min. All data reduction and structure refinement were done by using a modified Enraf-Nonius structure determintion package on a VAX 11/780 computer. Only the 2116 independent reflections with intensities greater than 3 times their esd's were used in the least-squares refinement.

The manganese atom was located from a three-dimensional Patterson map. Two cycles of least squares refinement based on the manganese atom position, followed by a difference Fourier map, revealed the locations of the phosphorus atom and eight carbon atoms. Two further cycles of least-squares, followed by a difference Fourier map, revealed the positions of the remaining non-hydrogen atoms. These coordinates were improved by two addditional cycles of isotropic least-squares refinement to give agreement indices of $R = 0.087$ and $R_w = 0.119$. Anisotropic parameters were then included, and several least squares cycles led to indices of $R = 0.060$ and $R_w = 0.090$. A total of 20 hydrogen atoms were found from difference Fourier maps. The remaining 11 hydrogen atoms were added at idealized positions with C-H bond distance of 0.95 Å. Isotropic thermal parameters for all of the hydrogen atoms were fixed at $B = 5.0$ Å^2. Continued anisotropic refinement of the non-hydrogen atoms led to final convergence with $R = 0.042$ and $R_w = 0.053$. Listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, and observed and calculated structure factor amplitudes are available as supplementary material.

(8) The structure is similar to that of bis(η^4-butadiene)(trimethyl phosphite)manganese recently reported by Wreford et al.: Harlow, R. L.; Krusic, P. J.; McKinney, R. J.; Wreford, S. S. *Organometallics* **1982**, *1*, 1506.

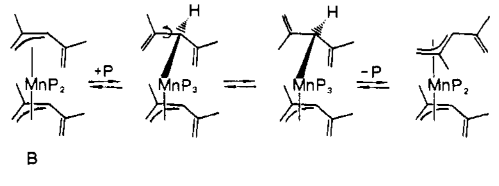
(9) The displacement of atoms C4′ and C7′ is due to a combination of two factors: (a) The strain introduced by the bridging ethylene group causes a disruption of the trigonal (sp^2) geometry around C4 and C7. (b) There is steric interaction between the methyl groups bonded to C4 and C7 and the methyl groups on the trimethylphosphine ligand.

(10) We wish to thank one of the reviewers for pointing out that disorder of this type is common in $-CH_2CH_2-$ linkages and would account for the anomalously short C5–C6 distance. However, our attempts to detect the disorder, using the following procedure, failed. We removed atoms C5, C6, H51, H52, H61, and H62 from the atoms list, performed two cycles of anisotropic least-squares refinement on the positions of the remaining non-hydrogen atoms, and then calculated a difference Fourier map. Even with a very small grid size (0.1 Å), the difference Fourier map revealed only two peaks in the ethylene bridge region (at the approximate positions which we have reported for C5 and C6).

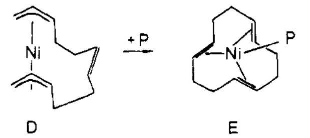
(11) (η^4-Butadiene)metal complexes generally exhibit shorter M–internal carbon distances than M–terminal carbon distances: Cotton, F. A.; Day, V. W.; Frenz, B. A.; Hardcastle, K. I.; Troup, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 4522.

(12) When $MnBr_2$ is reacted with potassium 3-methylpentadienide in the *absence* of $P(CH_3)_3$, an unusual trimetallic complex is produced: Wilson, D. R.; Liu, J.-Z.; Ernst, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 1120. "Open manganocene" has also been proposed as a low-temperature intermediate in this reaction.

(13) The anti to syn conversion probably involves a (σ-pentadienyl)manganese intermediate. A mechanism for the isomerization of the top η^3-pentadienyl group in B is proposed in the scheme below; an identical isomerization of the bottom η^3-pentadienyl ligand would lead to C.



Scheme II



D E

Coupling of the terminal carbon atoms of the two η^3-pentadienyl ligands in C leads to the isolated product **1**.

Although this proposed mechanism is speculative, several of its steps have precedent in the nickel-catalyzed butadiene cyclotrimerization reaction studied by Wilke.[14] In the nickel system, the *anti,anti*-bis(η^3-allyl-C_{12})nickel complex, D in Scheme II, can be isolated. Upon addition of trialkylphosphine, the two allylic moieties couple, and the cyclododecatriene ligand of the isolated cyclododecatriene(trialkylphosphine)nickel product E possesses three trans double bonds. The stereochemistry of the cyclododecatriene ligand implies that the *anti,anti*-bis(η^3-allyl-C_{12})nickel complex, D, converts to its syn,syn isomer before the coupling of the allylic ligands occurs.

Compound **1** reacts with mild oxidizing agents such as $AgPF_6$ to form isolable cationic complexes in the absence or presence of Lewis bases. The chemistry of these cations will be reported in a future communication.

The manganese-centered pentadienyl coupling reaction reported here illustrates the versatility of the acyclic pentadienyl ligand and the rich reaction chemistry that results from the pentadienyl ligand's ability to adopt a variety of bonding modes. We are continuing to investigate this and other pentadienylmetal–phosphine reaction systems.

Acknowledgment. We gratefully acknowledge Research Corp. for providing the funds (Cottrell Research Grant to J.R.B.) to purchase an inert atmosphere drybox. We thank Professor G. G. Stanley for assistance with the single-crystal X-ray diffraction study of **1** and R. A. Berger for his help in obtaining the mass spectrum of **1**.

Registry No. 1, 86508-10-3; $MnBr_2$, 13446-03-2; potassium 2,4-dimethylpentadienide, 74205-98-4.

Supplementary Material Available: Listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, and observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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[14] Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1975; Vol. 2, pp 134–141.

Aryldiazenido Complexes. Hydroxycarbonyl and Hydrido Derivatives of the Dicarbonyl(η-cyclopentadienyl)(aryldiazenido)rhenium Cation

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Summary: The cationic aryldiazenido complexes [(η-C_5H_5)Re(CO)$_2$(p-$N_2C_6H_4R$)][BF_4] (R = Me, OMe, or NEt_2) react with equimolar aqueous 0.1 M NaOH to give the air-stable, microcrystalline hydroxycarbonyl complexes (or metallocarboxylic acids) (η-C_5H_5)Re(CO)(p-$N_2C_6H_4R$)(COOH) and with excess 5 M KOH in H_2O–diethyl ether to give the air-stable hydrido complexes (η-C_5H_5)ReH(CO)(p-$N_2C_6H_4R$). These new hydroxycarbonyl and hydrido complexes are aryldiazenido analogues of the nitrosyl compounds (η-C_5H_5)Re(CO)(NO)(COOH) and (η-C_5H_5)ReH(CO)(NO) recently reported to be formed by action of base on the cationic complex [(η-C_5H_5)Re(CO)$_2$(NO)][BF_4] and exhibit comparable stability and spectroscopic properties, suggesting a similar influence of the nitrosyl and aryldiazenido ligands in the two series.

The corresponding complex cations [(η-C_5H_5)Re(CO)$_2$(NO)]$^+$ (**1**) and [(η-C_5H_5)Re(CO)$_2$(N_2Ar)]$^+$ (**2**) (Ar = aryl) potentially offer a good opportunity to compare the properties of the nitrosyl and aryldiazenido (N_2Ar) ligands and their influence on the reactions of the dicarbonyl(η-cyclopentadienyl)rhenium group. This is provided, of course, that the ligand itself is not the site of reaction. Unfortunately, in several reactions of **2** this happens to be the case. A particularly striking example is the action of $NaBH_4$, which converts **2** to the dicarbonyl aryldiazene complex (η-C_5H_5)Re(CO)$_2$(NHNAr), whereas in **1** a carbonyl group is reduced, leaving the nitrosyl group intact.[1,2]

In view of this, we now wish to report the reactions of **2a–c** with hydroxide ion, where we have observed a close correspondence with the chemistry recently reported by Sweet and Graham[3] for **1**. Furthermore, under appropriate conditions the products are, similarly, isolable, stable hydroxycarbonyl complexes, MCO_2H (or metallocarboxylic acids) which are therefore of considerable interest in view of the present scarcity of well-characterized compounds containing this functional group.[2d,3-8]

These new hydroxycarbonyl complexes (η-C_5H_5)Re(CO)(N_2Ar)(COOH) (**3a–c**) were synthesized by the dropwise addition under nitrogen of an equimolar quantity of aqueous 0.1 M NaOH to a stirred suspension of **2a–c** in water at room temperature. This gave yellow-orange solutions from which the products **3a–c** precipitated as analytically pure, golden yellow, air-stable, microcrystalline solids in ca. 95% yield,[9a] which are slightly soluble in water, giving bright yellow solutions. Their spectroscopic properties are those expected for formulation as hydroxycarbonyl complexes and compare with those of (η-C_5H_5)Re(CO)(NO)(COOH).[3] A strong terminal ν(CO) band

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[1] Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2578.

[2] (a) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811. (b) Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1979**, *173*, C9. (c) Tam, W.; Wong, W.-K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1578. (d) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *Ibid.* **1979**, *101*, 741.

[3] Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982.

[4] Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 443.

[5] Appleton, T. G.; Bennett, M. A. *J. Organomet. Chem.* **1973**, *55*, C88.

[6] Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627.

[7] Catellani, M.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 566.

[8] Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

[9] For example, **3a**: mp 102–104 °C dec; IR (CH_2Cl_2) 1954 (vs) (ν(CO)), 1643 (vs), 1596 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.45 (s, 3 H, CH_3), 5.83 (s, 5 H, C_5H_5), 7.25 (s, 4 H, C_6H_4), 8.9 (br s, 1 H, COOH). Anal. Calcd for $C_{14}H_{13}N_2O_3Re$: C, 37.92; H, 2.93; N, 6.32. Found: C, 37.77; H, 2.89; N, 6.27. ν(OH) was not observable directly in CH_2Cl_2, fluorolube mull, or KBr spectra of **3a–c**; ν(OD) was observed as a medium-weak broad band at 2240 cm^{-1} in a fluorolube mull spectrum of **3c** synthesized from NaOD in D_2O, giving a calculated ν(OH) near 3150 cm^{-1}. A weak band near 3450 cm^{-1} in **3a–c** showed no deuterium exchange.

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