Table I. Spectroscopic Data of Isolated Complexes

		IR,[a] ν_{CO} (cm^{-1})	^{1}H NMR,[b] δ (Me_4Si)
$FeCo(CO)_7(CHCH_2)$	1	2098 w, 2051 sh, 2045 s, 2037 m, 2017 s, 1980 w	CH, 7.95 dd (J_1 = 8Hz, J_2 = 13 Hz) CH_2, 3.05 d (J = 13 Hz), 2.82 d (J = 8 Hz)
$[CH_3CFeCo_2(CO)_9][P(C_6H_5)_4]$	2	2050 w, 1982 s, 1970 sh, 1915 w (br)	CH_3, 3.72
$CH_3CFeCo_2(CO)_9H$		2100 m, 2063 sh, 2052 s, 2047 s, 2036 s, 2012 m, 1988 m	CH_3, 2.58 d (J = 2.6 Hz); H, −9.80 (br)
$CH_3CCo_3(CO)_9$		2102 m, 2050 s, 2037 s, 2018 m	CH_3, 3.18
$CH_2CFeCo_2(CO)_9$	3	2102 m, 2053 s, 2047 s, 2037 s, 2015 m, 1987 m	CH_2, 3.78 (^{13}C NMR CO, 204.1 ppm, CH_2, 79.5 (J_{CH} = 162 Hz))
$CH_3CFe_2Co(CO)_{10}$	4	2098 w, 2047 s, 2030 s, 2008 m, 1840 w	CH_3, 4.08

[a] Hexadecane solutions except 2 (CH_2Cl_2 solution). [b] C_6D_6 solutions except 2 ($(CD_3)_2CO$ solution).

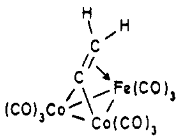

Figure 2. Proposed structure for complex 3.

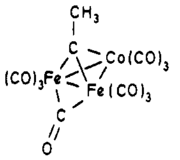

Figure 3. Proposed structure for complex 4.

$$FeCo(CO)_7CHCH_2 + Co(CO)_4^- \rightarrow [FeCo_2(CO)_9CCH_3]^- + 2CO \quad (3)$$

As complex 1 is quite easily accessible (ca. 50% yield), its thermal stability has been checked. Considerable redistribution is observed upon refluxing a solution hexane of 1 for 1 h. The proton NMR spectrum of the resulting mixture shows the presence of three new products while 1 has disappeared. The three products have been separated by chromatography on Florisil. The first product isolated is the pink $CH_3CCo_3(CO)_9$ identified by infrared and NMR spectra compared with literature data.[6,7] The second product is the brown solid 3 which crystallizes in hexane. Its infrared spectrum in the CO terminal stretching region is quite complex and very similar to that of the compound described as $H_2Fe_2Co(CO)_9CCH_3$.[8] Nevertheless, the proton NMR spectrum shows no hydride resonance. 3 has been identified by its mass spectrum. The parent ion has an m/z value of 452, and the ions corresponding to the successive loss of nine CO's are observed. The other ions observed have m/z values of 200 and 174, respectively. The latter corresponds to the ion $FeCo_2$, and the difference of 26 between these two ions corresponds to a C_2H_2 group. The formula of 3 is therefore $FeCo_2(CO)_9C_2H_2$, and the exact nature of the C_2H_2 group is ascertained by a gated ^{13}C NMR spectrum which shows a triplet at 79.5 ppm (J_{CH} = 162 Hz). From this observation, we conclude that the C_2H_2 group is a vinylalkylidene ligand and the structure shown in Figure 2, which is consistent with the proton NMR spectrum, is proposed for 3.

The third product, which is less abundant, is the brown solid 4. The presence of bridging CO's is observed in the CO stretching region of the infrared spectra (Table I), and the proton NMR spectrum shows no hydride resonance. 4 has also been identified by its mass spectrum. A parent ion with an m/z value of 478, and the ions corresponding to the successive loss of 10 CO's are observed. The other ions are Fe_2Co (m/z 171), Fe_2CoC (m/z 182), Fe_2CoC_2H (m/z 196), and $Fe_2CoC_2H_3$ (m/z 198). From these observations, we can conclude that the formula of 4 is $Fe_2Co(CO)_{10}CCH_3$. Its proposed structure is shown in Figure 3.

Thus, thermal rearrangement of 1 is seen to lead to trinuclear cluster units resulting from the scrambling of the two metals in one homonuclear tricobalt cluster and two heteronuclear clusters with an $FeCo_2$ or Fe_2Co core. Furthermore, the vinyl ligand generated both a vinylalkylidene (complex 3) and an ethylidyne ligand (complex 4) which stabilize the $FeCo_2$ and the Fe_2Co cores. Such rearrangements of vinyl groups are commonly encountered in cluster chemistry[9] but usually with second- and third-period metals.

Acknowledgment. This work has been supported by the CNRS (ATP Chimie Fine). J. R. thanks the Spanish Ministry of Education and Science for a fellowship. We thank Mr. Roussel for assistance in obtaining mass spectra and Mr. Commenges for the ^{13}C NMR spectra.

Registry No. 1, 85236-19-7; 2, 85236-21-1; 3, 85249-99-6; 4, 85236-22-2; $Co_2(CO)_8$, 10210-68-1; $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CHCH_2)][P(C_6H_5)_4]$, 85236-24-4; $Co(CO)_4^-$, 14971-27-8; $CH_3CFeCo_2(CO)_9H$, 69493-75-0; $CH_3CCo_3(CO)_9$, 13682-04-7; Co, 7440-48-4; Fe, 7439-89-6.

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Apparent Syn Elimination of Palladium Oxide from a β-Hydroxy Organopalladium Intermediate

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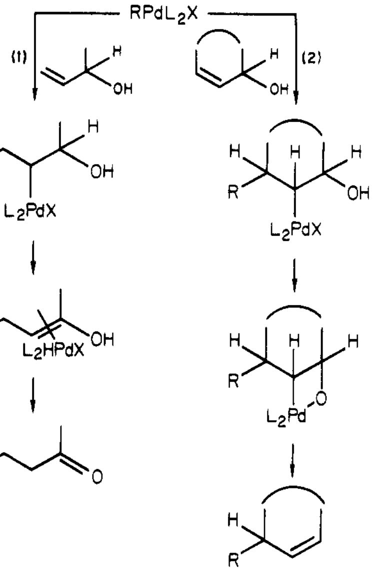
Received January 19, 1983

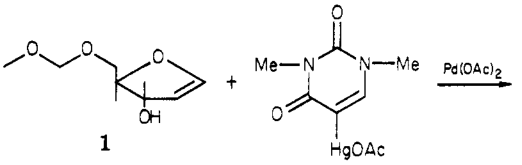
Summary: Reaction of 1,4-anhydro-2-deoxy-5-*O*-(methoxymethyl)-D-*erythro*-pent-1-enitol (**1**) with (1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)mercuric acetate (**2**) in the presence of palladium(II) acetate forms an adduct which possesses adjacent cis hydroxyl and palladium(II) substituents. The observed decomposition of this adduct to (2′-*S*-*trans*)-5-[2′,5′-dihydro-5′-[(methoxymethoxy)methyl]-2′-furanyl]-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione is most reasonably formulated as involving

a palladaoxabutane intermediate which undergoes ring scission to the olefinic product and palladium oxide.

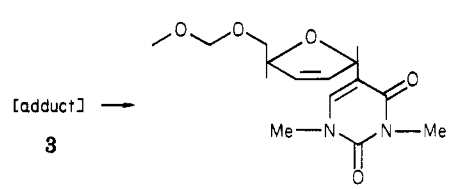
Reactions of (σ-organo)palladium(II) reagents with acyclic allylic alcohols involve formation of (β-hydroxy-σ-organo)palladium adducts which decompose by initial syn β-hydride elimination from the oxygen-bearing carbon to yield 3-substituted aldehydes or ketones (eq 1).[1] We wish to report that when syn hydridopalladium elimination (and other facile processes; *anti*-acetoxy- or *anti*-alkoxy-palladium eliminations)[2-4] are precluded, e.g., by ring formation and/or substitution, such organopalladium adducts can apparently undergo syn elimination of palladium oxide (eq 2). To our knowledge this reaction (eq 2) has not been observed previously in organopalladium chemistry.



In extension of our studies of palladium-mediated reactions of pyranoid glycals with organomercurials,[3,5] directed toward development of a new general synthesis of *C*-nucleosides (glycosides),[6] we have investigated the corresponding reactions of certain furanoid glycals. Addition of 1.3 equiv of 1,4-anhydro-2-deoxy-5-*O*-(methoxymethyl)-D-*erythro*-pent-1-enitol[7] (**1**) to an acetonitrile solution of (1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)mercuric acetate[5] and palladium(II) acetate resulted in formation of a relatively stable organopalladium adduct (**3**). This adduct decomposed thermally (70 °C, 8 h) affording (2′-*S*-*trans*)-5-[2′,5′-dihydro-5′-[(methoxymethoxy)methyl]-2′-furanyl]-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione (**4**)[8,9] in 35% yield. Addition of base (sodium bicarbonate or diisopropylethylamine, 3 equiv) to the reaction mixture facilitated adduct decomposition under mild conditions (room temperature, 3 days) and gave a higher yield (75%) of **4**.



1 **2**



3 **4**

The structure of product **4** was determined as follows. The large 1′H, 4′H coupling constant (J = 5.8 Hz) in the ^{1}H NMR spectrum of **4**[8,9] is indicative of a trans relationship between the 1′ and 4′ substituents of the carbohydrate ring.[10,11] The trans relationship of these substituents was established rigorously by the following chemical transformations. Compound **4** was dihydroxylated (catalytic OsO_4/*t*-BuOH, trimethylamine *N*-oxide, 1 equiv, acetone; room temperature, 24 h) affording a mixture of diols which, without isolation, was converted to the corresponding mixture of acetonides (catalytic *p*-toluenesulfonic acid, 2,2-dimethoxypropane, 3 equiv, acetone; room temperature, 12 h) to give an 8:2 mixture of 5-[5′-*O*′(methoxymethyl)-2′,3′-*O*-(1-methylethylidene)-α-D-ribofuranosyl]-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione (**5**)[12] and 5-[5′-*O*-(methoxymethyl)-2′,3′-*O*-(methylethylidene)-α-D-lyxofuranosyl]-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione (**6**)[12] in essentially quantita-

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(1) (a) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5526. (b) Melpolder, J. B.; Heck, R. F. *J. Org. Chem.* **1976**, *41*, 265. (c) Chalk, A. J.; Magennis, S. A. *Ibid.* **1976**, *41*, 273. (d) Von Werner, K. *J. Organomet. Chem.* **1977**, *136*, 385. (e) Tamaru, Y.; Yamada, Y.; Yoshida, Z.-I. *Tetrahedron Lett.* **1977**, 3365. (f) Tamaru, Y.; Yamada, Y.; Yoshida, Z.-I. *J. Org. Chem.* **1978**, *43*, 3396. (g) Patel, B. A.; Heck, R. F. *Ibid.* **1978**, *43*, 3898. (h) Tamaru, Y.; Yamada, Y.; Yoshida, Z.-I. *Tetrahedron* **1979**, *35*, 329. (i) Smadja, W.; Czernecki, S.; Ville, G.; Georgoulis, C. *Tetrahedron Lett.* **1981**, *22*, 2479. (j) Kao, L.-C.; Stakem, F. G.; Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1982**, *47*, 1267.

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(3) (a) Arai, I.; Daves, G. D., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 7683. (b) Arai, I.; Lee, T. D.; Hanna, R.; Daves, G. D., Jr. *Organometallics* **1982**, *1*, 742.

(4) (a) Bäckvall, J. E.; Åkermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411. (b) Åkermark, B.; Bäckvall, J. E.; Zetterberg, K. *Acta Chem. Scand., Ser. B* **1982**, *B36*, 577.

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(6) (a) Daves, G. D., Jr.; Cheng, C. C. *Prog. Med. Chem.* **1976**, *13*, 303. (b) Hannessian, S.; Pernet, A. G. *Adv. Carbohydr. Chem. Biochem.* **1976**, *3*, 111. (c) Fox, J. J.; Watanabe, K. A.; Klein, R. S.; Chu, C. K.; Tam, S. Y.-K.; Reichman, U.; Hirota, K.; Wempen, I.; Lopez, C.; Burchenal, J. H. *Colloq.—Inst. Natl. Sante Rech. Med.* **1978**, *81*, 241.

(7) (a) Ireland, R. E.; Wilcox, C. S.; Thaisrivongs, S. *J. Org. Chem.* **1978**, *43*, 786. (b) Ireland, R. E.; Thaisrivongs, S.; Vanier, N.; Wilcox, C. S. *Ibid.* **1980**, *45*, 48.

(8) All the compounds reported exhibit ^{1}H, ^{13}C NMR, and mass spectra in agreement with the assigned structures. For convenience, we use the common carbohydrate numbering system (the anomeric carbon is designated 1′) in discussions of spectra and structural features.

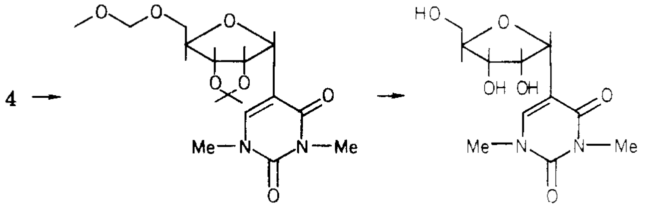
(9) ^{1}H NMR (C_6D_6) δ 2.71, 3.22, 3.24 (NMes, OMe), 3.57 (5′Hs, d), 4.58 (OCH_2O, s), 5.06 (4′H, m), 5.67 (3′H, m), 5.87 (1′H, m), 6.24 (2′H, m), 6.84 (6H, d), $J_{1'H,4'H}$ = 5.8 Hz. Resonances and coupling constant assignments are based on extensive spin–spin decoupling experiments and were confirmed by spin–spin stimulation.

(10) Barfield, M.; Spear, R. J.; Sternhell, S. *J. Am. Chem. Soc.* **1975**, *97*, 5160 and references cited therein.

(11) $J_{1'H,4'H}$ has been reported as ~1.5 Hz for 2′,3′-didehydro-2′,3′-dideoxy-1-methyl-5′-*O*-trityl-β-pseudouridine in which the 1′ and 4′ substituents are cis. Matsuda, A.; Chu, C. K.; Reichman, U.; Pankiewicz, K.; Watanabe, K. A.; Fox, J. J. *J. Org. Chem.* **1981**, *46*, 3603.

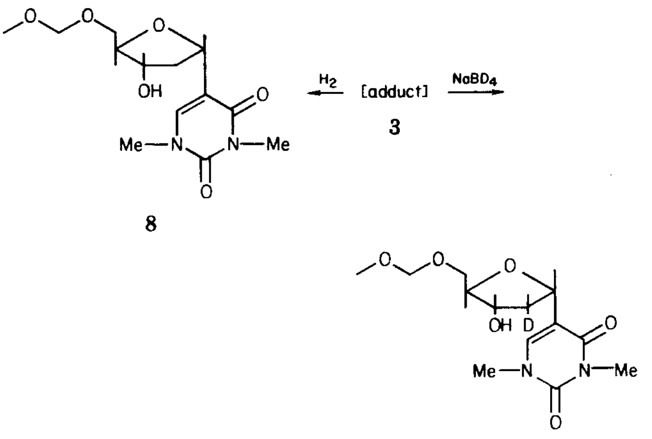
(12) The relative configurations at C1′, C2′, C3′, and C4′ of **5** and **6** was determined by using well-documented empirical rules that correlate chemical shifts in ^{1}H and ^{13}C NMR of the isopropylidene unit with the α or β configuration of nucleosides. See, e.g.: (a) Imbach, J. L. *An. N.Y. Acad. Sci.* **1975**, *255*, 177. (b) Ohrui, H.; Jones, G. H.; Moffat, J. G.; Maddox, M. L.; Christensen, A. T.; Byram, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 4602. (c) Cousineau, T. J.; Secrist, J. A., III *J. Org. Chem.* **1979**, *24*, 4351.

tive yield. Chromatographic separation of **5** followed by deprotection ($MeOH/H_2O/HCl$; room temperature, 2 h, 80%) gave 1,3-dimethyl-α-pseudouridine (**7**)[13] which was indistinguishable from an authenic sample,[14] thus unambigously establishing the configuration and structure of **4**.



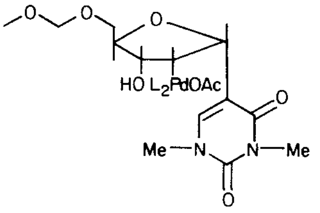
5 **7**

To account for the formation of product **4**, it is necessary to establish the structure of adduct **3** which we have been unable to isolate or purify.[15] Adduct **3** must result from regiospecific syn addition[16] of the pyrimidinylpalladium reagent formed by transmetalation of **2**[2] to the furanoid glycal (**1**) enol ether double bond. Two lines of evidence identify the attack of the organopalladium reagent as occurring on the hydroxyl-bearing, α face of **1**. The trans relationship of the 1′ and 4′ substituents of product **4** was unambiguously established (see above). Further, shaking a reaction mixture containing adduct **3** under hydrogen (2 atm) for 8 h produced 2′-deoxy-1,3-dimethyl-5′-*O*-(methoxymethyl)-α-pseudouridine (**8**,[17a] 76%), and reduction of adduct **3** in situ, using sodium borodeuteride, afforded **9**[17b] (17%) in which the α-2′-hydrogen of **8** is replaced by a deuterium. Thus, although the intermediate adduct has not been isolated and purified,[15] it is clear that it possesses structure **3**, in which the 1′-pyrimidinyl, 2′-palladium(II), and 3′-oxygen substituents all occupy the α face of the furanoid ring.[18]

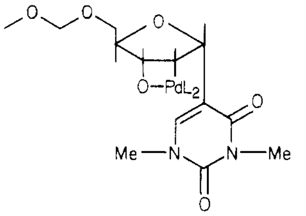


8 **3** **9**

Decomposition of adduct **3** is complicated by the fact that previously identified decomposition modes[2-4] are precluded; i.e., **3** possesses no β-hydrogens cis to palladium[3] and no β-acetoxy[3] (or hydroxy)[4] groups trans to Pd and the conformational rigidity of the furanoid ring disfavors the anti periplanar disposition of ring oxygen and palladium associated with elimination of palladium and ring opening.[3] The formation of **4** from adduct **3** requires the elimination of adjacent cis hydroxyl and palladium(II) substituents.[18] This process is most reasonably formulated[19] as initially involving metallaoxacyclobutane formation by loss of the elements of acetic acid (hydroxyl proton and acetoxy ligand) to form a secondary palladium adduct **3b** which decomposes to yield olefin **4** and palladium oxide. The sensitivity of the initially formed adduct **3a** to added base is consistent with the intermediacy of palladaoxacyclobutane adduct **3b** in the decomposition pathway.



3a



3b

Metallaoxacyclobutane intermediates have been suggested previously—in the reduction of epoxides to olefins by dilithium hexachlorotungstenate[20] and in the epoxidation of olefins by chromyl chloride[20] or by bis(acetonitrile)chloronitropalladium(II)[21]. Furthermore, platinum metallaoxacyclobutane derivatives have been isolated and their structure established by X-ray crystallography.[22] Precedents for the postulated ring scission exist in organophosphorous[23] and organosulfur chemistry.[24]

The industrially important Wacker process, which takes place under strongly acidic conditions, involves a reversible, anti hydroxy palladation step.[19] In contrast, the syn elimination of palladium oxide observed here occurs readily

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[13] ^{1}H NMR (D_2O): δ 3.29, 3.45 (Mes), 3.55–4.10 (4′H, 5′Hs, m), 4.22–4.45 (2′H, 3′H, m), 4.75 (OHs, obscured by H_2O), 5.05 (1′H, m), 7.64 (6 H, d).

[14] Prepared from α-pseudouridine (Sigma) using dimethylformamide dimethyl acetal according to: Hirota, K.; Watanabe, K. A.; Fox, J. J. *J. Heterocycl. Chem.* **1977**, *14*, 537.

[15] Mass spectra (fast atom bombardment) of the crude reaction mixture containing adduct **3** exhibit ion clusters at *m/z* 446 (^{106}Pd isotope) corresponding to (a) [**3a**-LOAc]$^+$ or (b) [**3b**-L+H$^+$]$^+$. In mass spectrometry using a soft ionization technique observed ions are preformed (a) or formed by protonation (b); as a result, no distinction between structures **3a** and **3b** is possible (see: Cotter, R. J. *Anal. Chem.* **1980**, *52*, 1589A. Daves, G. D., Jr. *Acc. Chem. Res.* **1979**, *12*, 359).

[16] All additions of organopalladium reagents to double bonds which have been carefully examined have been shown to be syn; no example of anti addition of a carbon σ-bonded palladium reagent is known (See: Henry, P. M.; Ward, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 673 and ref 2 and 4). In our closely related studies using pyranoid glycals[3] syn addition of the palladium reagent derived from **2** has been established conclusively.

[17] (a) ^{1}H NMR ($CDCl_3$): δ 1.85–2.12 (α-2′H, m), 2.55–2.90 (β-2′H, m), 3.34, 3.37, 3.41 (NMes, OMe), 3.59 (5′Hs, m); 4.12–4.45 (3′H, 4′H, m), 4.65 (OCH_2O, s), 4.85 (1′H, dd), 7.33 (6 H, br s). Mass spectrum: *m/z* 300 (M$^{+\cdot}$). (b) ^{1}H NMR ($CDCl_3$): δ 2.70 (β-2′H, dd), 3.33, 3.36, 3.40 (NMes, OMe), 3.57 (5′Hs, m), 4.05–4.45 (3′H, 4′H, m), 4.63 (OCH_2O, s), 4.85 (1′H, d), 7.30 (6 H, br s). Mass spectrum: *m/z* 301 (M$^{+\cdot}$).

[18] The unlikely possibility that **4** arises via a (η^3-allyl)palladium complex derived from **1** is ruled out by the establishment that the intermediate adduct (**3**) possesses both carbon bound oxygen at C-3 and palladium. For relevant studies of (η^3-allyl)palladium chemistry see: Trost, B. M. *Pure Appl. Chem.* **1981**, *53*, 2357. Matsushita, H.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1982**, *160*. Dunkerton, L. V.; Serino, A. J. *J. Org. Chem.* **1982**, *47*, 2812. Similarly, the possibilities that **4** arises from **3a** by (a) hydroxyl acetylation and subsequent syn elimination of palladium acetate (suggested by a reviewer) or (b) hydroxyl displacement by acetate followed by anti elimination of palladium acetate appear remote since mass spectrometry[15] and reduction of crude reaction mixtures indicate the presence of **3a** but provide no evidence for an acetoxy analogue. Addition (but not elimination) of acetate syn to palladium in η^3-alkyl complexation has been observed: Bäckvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 4959. Trost, B. M.; Verhoeven, T. R. *Ibid.* **1980**, *102*, 4730.

[19] Compare ref 4. See, however: Gregor, N.; Henry, P. M. *J. Am. Chem. Soc.* **1981**, *103*, 681. Wan, W. K.; Zaw, K.; Henry, P. M. *J. Mol. Catal.* **1982**, *16*, 81.

[20] Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120.

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[24] Corey, E. J.; Durst, T. *J. Am. Chem. Soc.* **1968**, *90*, 5548.

in weakly basic media. It is noteworthy that β-hydroxy-substituted organosilanes,[25] organostannanes,[26] and organoplumbanes[26] exhibit anti elimination under acidic conditions but undergo syn elimination thermally or with base catalysis.

Acknowledgment. Financial support of this work from the National Institute of General Medical Science (Grant GM 30310), from S. Söderlundhs Minnesfond, and from Thuns fond is greatly appreciated. William R. Anderson, Jr., and Henry Kalinoski provided mass spectra; we thank Lars-Erik Arvidsson for preliminary experiments.

Registry No. 1, 72050-15-8; 2, 65904-27-0; 3a, 85442-28-0; 3b, 85442-30-4; 4, 85442-29-1; 5, 85442-23-5; 6, 85442-24-6; 7, 85442-25-7; 8, 85442-26-8; 9, 85442-27-9.

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(25) Hudrlik, P. F.; Peterson, D.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2263.

(26) Kauffmann, T.; Kriegesmann, R.; Hamsen, A. *Chem. Ber.* **1982**, *115*, 1818.

Formation and Characterization of the Persistent Rhenium Radical Bis(tricyclohexylphosphine)tricarbonylrhenium(0)

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Summary: The first example of a persistent rhenium(0) radical, $Re(CO)_3(P\text{-}c\text{-}Hx_3)_2\cdot$, has been prepared and characterized in benzene solution, by extended photolysis of $Re_2(CO)_8(P\text{-}c\text{-}Hx_3)_2$ in the presence of excess P-c-Hx_3, with removal of CO. EPR, IR, and UV–visible spectra have been obtained.

Radicals of the type $Re(CO)_{5-n}L_n\cdot$ (L = phosphorus donor ligand) have been proposed as intermediates in the thermal and photochemical substitution reactions of $HRe(CO)_5$[1] and $Re_2(CO)_{10}$.[2-4] Earlier claims of stable $Re(CO)_3L_2\cdot$ radicals[5,6] have been shown to be incorrect; the products formed proved to be diamagnetic compounds.[4a,7,8] Recent reported attempts to produce persistent rhenium radicals have been unsuccessful.[4a] In general, formation of persistent rhenium radicals will be difficult because of the greater ease of metal–metal bond formation and greater driving force for atom abstraction from solvent as compared with manganese. We report here the first example of a persistent metal-centered substituted rhenium carbonyl radical, $Re(CO)_3(P\text{-}c\text{-}Hx_3)_2$. (P-c-$Hx_3$ = tricyclohexylphosphine). The unique stability of this radical is ascribable to the large cone angle of the phosphine.[9]

Table I. EPR Spin-Hamiltonian Parameters of $Re(CO)_3(P_3)_2\cdot$ in Frozen Benzene at 77 K

	axis[a]	g	$A_{Re}/g\beta$,[b] G	$A_P/g\beta$, G
major species	∥	1.9782	412	14.2
	⊥	2.1257	78.7	14.2
minor species	∥	1.9784	310	

[a] Axial symmetry has been assumed pending further refinement. [b] 1 G = 10^{-4} T.

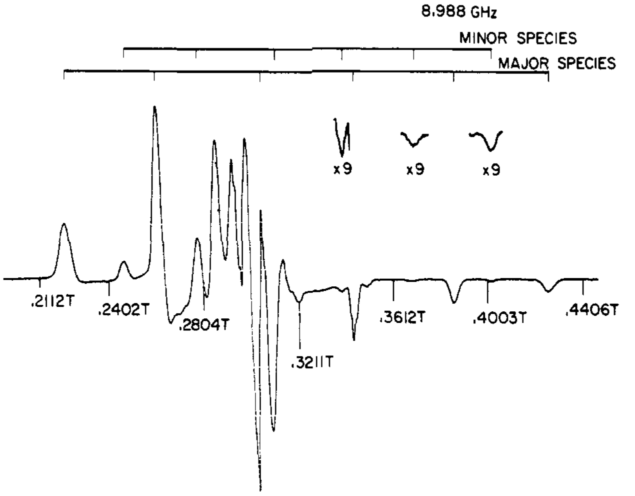

Figure 1. EPR spectrum of a frozen benzene solution (77 K) of $Re(CO)_3(P\text{-}c\text{-}Hx_3)_2\cdot$. Parallel-field transitions for both major and minor species are indicated.

We have previously described the formation and properties of $Mn(CO)_3L_2\cdot$ (L = phosphorus donor ligand) radicals[10] and have studied the hydrogen atom transfer[11] and ligand substitution reactions.[12] Formation of $Re(CO)_3(P\text{-}c\text{-}Hx_3)_2\cdot$ is accomplished in a manner similar to that described for the manganese radicals. A benzene solution of $Re_2(CO)_8(P\text{-}c\text{-}Hx_3)_2$ (2.7 mM) and P-c-Hx_3 (9.5 mM) in a quartz photolysis tube is irradiated with unfiltered light form a GE sunlamp for 5 h. The solution is occasionally degassed by brief evacuation of the flask. Over the course of the photolysis, the initially colorless solution turns deep blue. A single new infrared absorption in the carbonyl region grows in at 1849 cm^{-1}. Upon exposure to air, the solution immediately loses its blue color and the IR band at 1849 cm^{-1} disappears. No new carbonyl peaks are observed. When CCl_4 is added to the solution, the blue color is lost, the IR band at 1849 cm^{-1} disappears, and new peaks appear at 1922 and 1873 cm^{-1}. These peaks are assigned to $Re(CO)_3(P\text{-}c\text{-}Hx_3)_2Cl$ in analogy with $Re(CO)_3(PPh_3)_2Cl$[13] which shows absorptions at 1930 and 1880 cm^{-1} with a weak peak at 2036 cm^{-1}.

The frozen solution 9-GHz EPR spectrum has been obtained at 77 K (Figure 1). The spin-Hamiltonian parameters obtained from a computer simulation[14] (prelim-

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