2 exhibit large Stokes shifts, and for **2** collection at the higher energy bands results in a different excitation spectrum from that of the lower energy band. In the solid state, both forms of **1** and **2** show intense, unstructured emissions at room temperature which increase modestly in intensity at 77 K, but with no development of appreciable structure. The solid state emission maxima are shifted to lower energy by ~800–1500 cm^{-1} relative to the solution values. For **1** the red and yellow forms exhibit different λ_{em}'s which shift to lower energies at 77 K as illustrated in Figure 2. In contrast, solid samples of **2** show no energy shift upon cooling to 77 K but do exhibit slightly increased emission intensity.

Relative quantum yields for solution emission of **1** and **2** were measured by using $[Ru(bpy)_3]^{2+}$ in DMF as a standard (Φ_{em} = 0.068).[7] For these measurements, solvents were rigorously dried, distilled, and degassed. In all solvents, the relative quantum yield for **2** was about an order of magnitude greater than for **1**. The values of Φ_{em} varied with solvent, ranging from 1.63×10^{-4} and 1.39×10^{-4} in acetone and DMF to 2.67×10^{-4} in CH_2Cl_2 for **1** and 1.33×10^{-3} and 1.95×10^{-3} in acetone and DMF to 2.69×10^{-3} in CH_2Cl_2 for **2**. In mixtures of CH_2Cl_2 and DMF, the quantum yield increased as a function of the solvent ratio.

Emission lifetimes of **1** and **2** were measured by single photon counting in fluid solution, frozen glass, and pure solid. Complex **2** was found to exhibit single exponential decay in CH_2Cl_2/DMF/MeOH fluid solution at 298 K (τ = 22 ns) and in frozen glass at 77 K (1.8 μs), but double exponential decay in the pure solid at 77 K (324 ns, 1.26 μs). In contrast, complex **1** shows multiple exponential decay in all samples run with values of τ, obtained from deconvolution, of 3.4 and 13.5 ns in fluid solution at 298 K, 16.4 and 109 ns for the solid yellow form, and 15.7 and 47.9 ns for the red form. In all three cases, a possible third component with a much shorter lifetime also exists (0.5–2 ns).[8]

Quenching studies of **2** in CH_2Cl_2 were performed by using the electron donor *N*,*N*-dimethylaniline (DMA) and the electron acceptor *o*-nitrobenzaldehyde (ONB). The concentration of **2** employed was 2×10^{-5} M while the concentrations of quencher ranged from 7.9×10^{-4} to 1.6×10^{-2} M for DMA and 1.1×10^{-2} to 6.7×10^{-2} M for ONB. Good Stern–Volmer plots were obtained in both cases with K_{SV} of 24.8 and 188 for ONB and DMA, respectively. The corresponding k_q values calculated from K_{SV} and the solution excited state lifetime of **2** are 6.8×10^8 and 9×10^9 M^{-1} s^{-1}, respectively. The nature of the quenching as electron transfer is supported by the electrochemistry and the fact that the triplet energies of both ONB (61 kcal/mol)[9] and DMA (74 kcal/mol)[10] are significantly larger than that estimated for **2** from its emission (52 kcal/mol). Consistent also with the electrochemistry is the fact that irradiation of **2** in the presence of DMA (1.6×10^{-2} M) yields no change in the absorption spectrum after 24 h whereas a sample containing ONB (1.1×10^{-2} M) shows bleaching of the 454-nm band over 5 h indicating degradation of the complex by irreversible oxidation.

The nature of the emissive state in these Pt(II) complexes is uncertain. However, the structureless emissions and the fact that no emission is observed for the Pd and Ni analogues provide evidence against an intra- or interligand excited state.[11] Moreover, related Pt(II) diimine complexes with chloride ligands (which are similar in ligand field strength to dithiolates[12]) have a ligand field (LF) state as the lowest energy transition, but they do not show the strong absorption band in the visible and only emit as solids at low temperature.[13] Based on this spectroscopic evidence and the electron-transfer quenching outlined above, we favor a charge-transfer excited state involving the metal center and the dithiolate ligand. However, the multiple lifetimes and emergence of new bands in the low-temperature emission spectrum of **2** (Figure 1) suggest more than one emitting state. With regard to the latter, these new bands are assigned to a dpphen-based IL (intraligand) emitting state similar to that found for Pt(N$\frown$N)Cl$_2$.[14]

The discovery of new compounds possessing long-lived excited states leads not only to a better understanding of photochemical and photophysical principles but also to development of new applications of light-induced reactions. In contrast to the well-studied $Ru(bpy)_3{}^{2+}$, the compounds described here are coordinatively unsaturated, making them good candidates as photocatalysts. On the basis of the experiments described above, reductive quenching of these complexes may permit direct reduction of H$^+$ and CO$_2$ at the metal center, and this possibility is under active investigation.

Acknowledgment. We thank Eastman Kodak Co., Inc., for a grant to help support this work, Dr. Mitch Burberry and Mark Prichard for help with the lifetime measurements, and Kurt Kramarz for help with the electrochemistry. A generous loan of platinum salts from Johnson Matthey Co. Inc. is also gratefully acknowledged.

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(14) The possibility of Pt(dpphen)Cl$_2$ as an impurity in the sample was eliminated by showing that the sample exhibited no spectral change after repeated recrystallizations and after being passed twice through a silica column with different solvent combinations. Moreover, the emission spectrum of Pt(dpphen)Cl$_2$ under conditions identical with those used for **2** is red shifted by ~20 nm.

Synthesis of Rhenium–Alkene Complexes from the Reaction of the Heterobimetallic Dihydride $C_5H_5(CO)_2HRe{-}PtH(PPh_3)_2$ with Alkynes

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Received July 14, 1989

Heterobimetallic compounds hold great promise as catalysts since the two different metals have the potential of acting cooperatively. However, since the problem of optimizing a system for each of two metals is an added complication, there are few examples of homogeneous heterobimetallic catalysts.[1] Here we report that the new heterobimetallic dihydride $C_5H_5(CO)_2HRe{-}PtH(PPh_3)_2$ (**1**)[2] acts as a catalyst for ethylene hydrogenation and reacts stoichiometrically with alkynes to produce rhenium–alkene complexes.

When the synthesis of **1** from *trans*-Cp(CO)$_2$ReH$_2$ (**2**) and $(CH_2{=}CH_2)Pt(PPh_3)_2$ (**3**) was carried out in a sealed NMR tube, we noticed the slow formation of small amounts of ethane. Consequently, we began a study of the hydrogenation of ethylene catalyzed by **1**. We found that **1** slowly catalyzed the hydrogenation of ethylene to ethane in benzene-d_6 at room temperature and 0.6 atm of H$_2$. After 2 days, the hydrogenation ceased after producing 4.2 equiv of ethane. When the reaction was monitored by ^{1}H NMR, we noted an initial reaction of **1** with ethylene that

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(1) (a) Dombek, B. D.; Harrison, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 2485. (b) Knifton, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 729. (c) Knifton, J. F.; Grigsby, R. A., Jr.; Lin, J. J. *Organometallics* **1984**, *3*, 62. (d) Whyman, R. *J. Chem. Soc., Chem. Commun.* **1983**, 1439. (e) Laine, R. M. *J. Org. Chem.* **1980**, *45*, 3370. (f) Hidai, M.; Fukuoka, A.; Koyasu, Y.; Uchida, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 516. (g) Hidai, M.; Fukuoka, A.; Koyasu, Y.; Uchida, Y. *J. Mol. Catal.* **1986**, *35*, 29. (h) Doyle, G. *J. Mol. Catal.* **1983**, *18*, 251. (i) Ceriotti, A.; Garlaschelli, L.; Longoni, G.; Malatesta, M. C.; Strumolo, D.; Fumagalli, A.; Martinengo, S. *J. Mol. Catal.* **1984**, *24*, 309.

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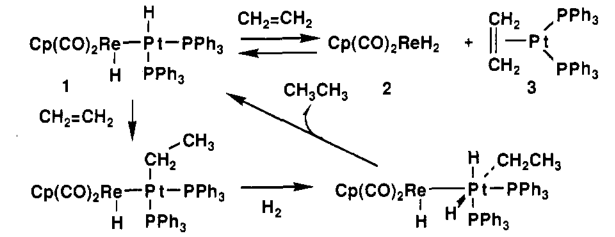
0002-7863/89/1511-8917$01.50/0

Scheme I

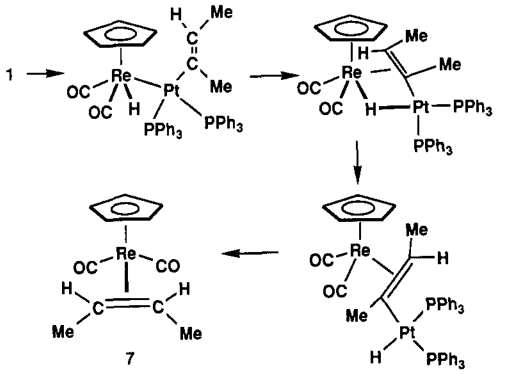


produced rhenium dihydride **2** and platinum–ethylene complex **3**. This is the reverse of the synthesis of **1** and demonstrates that **1** and ethylene are in equilibrium with **2** and **3** at room temperature. After loss of hydrogenation activity, the rhenium-containing products were a 3:1 mixture of $Cp(CO)_2Re(PPh_3)^3$:$Cp(CO)_2Re(CH_2{=}CH_2)$,[4,5] and the platinum-containing materials were a 1.2:1 ratio of **3**:$(Ph_3P)Pt(CH_2{=}CH_2)_2$.[6] Control experiments showed no ethylene hydrogenation in the presence of rhenium dihydride **2** alone and only extremely slow hydrogenation of ethylene (<0.3 equiv in 12 days) in the presence of platinum–ethylene complex **3**. One of the many possible mechanisms that take into account the need for both Re and Pt starts with bimetallic complex **1** and is shown in Scheme I.

Attempted catalytic hydrogenation of propyne with rhenium–platinum dihydride **1** failed to produce free propene. Instead, stoichiometric formation of rhenium–propene complex $C_5H_5(CO)_2Re(CH_2{=}CHCH_3)$ (**4**)[7] and platinum–propyne complex $(Ph_3P)_2Pt(HC{\equiv}CCH_3)$ (**5**)[8] was observed over 1 day. The rhenium–propene complex **4** is very thermally stable and was isolated in 99% yield based on **1** by column chromatography followed by sublimation at 50 °C. The failure of the alkene to dissociate from rhenium is one reason this hydrogenation is not catalytic in rhenium.[9] When the reaction of **1** with 2 equiv of propyne was monitored by ^1H NMR in CD_2Cl_2, initial rapid formation of an equilibrium mixture of **1** (40%), rhenium dihydride **2** (60%), and platinum–propyne complex **5** was observed. After 24 h, only rhenium–propene complex **4** and platinum–propyne **5** were seen. No reaction was observed between rhenium dihydride **2** and propyne in the absence of platinum compounds, but complete conversion of **2** to **4** was achieved in 2 days in the presence of 10% of the bimetallic catalyst **1**. Reaction of **1**-d_2 (87% deuterium formed by exchange with D_2)[2] with propyne led to clean cis hydrogenation in the formation of propene–complex **4**-d_2. In the ^2H NMR of **4**-d_2, two equal-intensity resonances were seen at δ 2.65 and 2.04 for the secondary vinyl deuterium and the primary vinyl deuterium trans to methyl; no resonance was seen at δ 1.82 for deuterium cis to methyl.

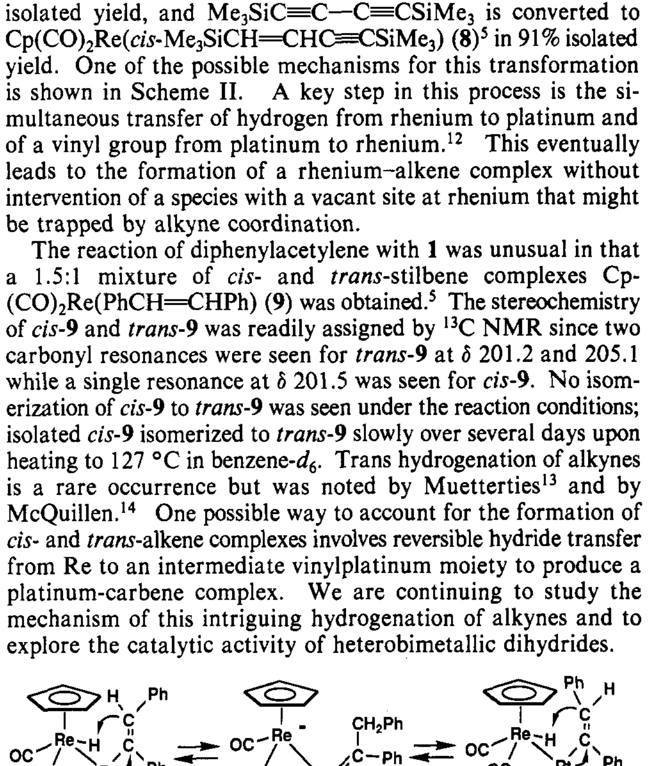
The reaction of **1** with propyne is the first example of a stoichiometric hydrogenation of an alkyne to a metal–alkene complex.

Scheme II



The reaction is quite general and is the most convenient preparation of pure rhenium–alkene complexes available.[11] For example, *tert*-butylacetylene is converted to $Cp(CO)_2Re(CH_2{=}CHCMe_3)$ (**6**)[5] in 67% isolated yield based on **1**, 2-butyne is converted to $Cp(CO)_2Re(\textit{cis}\text{-}CH_3CH{=}CHCH_3)$ (**7**)[5] in 91% isolated yield, and $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ is converted to $Cp(CO)_2Re(\textit{cis}\text{-}Me_3SiCH{=}CHC{\equiv}CSiMe_3)$ (**8**)[5] in 91% isolated yield. One of the possible mechanisms for this transformation is shown in Scheme II. A key step in this process is the simultaneous transfer of hydrogen from rhenium to platinum and of a vinyl group from platinum to rhenium.[12] This eventually leads to the formation of a rhenium–alkene complex without intervention of a species with a vacant site at rhenium that might be trapped by alkyne coordination.

The reaction of diphenylacetylene with **1** was unusual in that a 1.5:1 mixture of *cis*- and *trans*-stilbene complexes $Cp(CO)_2Re(PhCH{=}CHPh)$ (**9**) was obtained.[5] The stereochemistry of *cis*-**9** and *trans*-**9** was readily assigned by ^{13}C NMR since two carbonyl resonances were seen for *trans*-**9** at δ 201.2 and 205.1 while a single resonance at δ 201.5 was seen for *cis*-**9**. No isomerization of *cis*-**9** to *trans*-**9** was seen under the reaction conditions; isolated *cis*-**9** isomerized to *trans*-**9** slowly over several days upon heating to 127 °C in benzene-d_6. Trans hydrogenation of alkynes is a rare occurrence but was noted by Muetterties[13] and by McQuillen.[14] One possible way to account for the formation of *cis*- and *trans*-alkene complexes involves reversible hydride transfer from Re to an intermediate vinylplatinum moiety to produce a platinum-carbene complex. We are continuing to study the mechanism of this intriguing hydrogenation of alkynes and to explore the catalytic activity of heterobimetallic dihydrides.



Acknowledgment. Financial support from the Department of Energy, Division of Basic Energy Sciences, is gratefully ac-

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(3) (a) Nesmeyanov, A. N.; Kolobova, N. E.; Makarov, Yu. V.; Lokshin, B. V.; Rusach, E. B. *Isv. Akad. Nauk. SSSR, Ser. Khim.* **1976**, *3*. 629. (b) Yang, G. K.; Bergman, R. G. *Organometallics* **1985**, *4*, 129.

(4) $Cp(CO)_2Re(CH_2{=}CH_2)$ was preliminary reported as a product of the decomposition of the metallacyclopentane $Cp(CO)_2Re(CH_2)_4$ in the presence of $CH_2{=}CH_2$ but no characterization was given.[3b] We have prepared $Cp(CO)_2Re(CH_2{=}CH_2)$ from ethylene and $Cp(CO)_2Re(THF)$.

(5) See Supplementary Material for full characterization.

(6) Harrison, N. C.; Murray, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1337.

(7) For **4**: ^1H NMR (C_6D_6, 270 MHz) δ 4.38 (s, C_5H_5), 2.75 (ddq, $J_{trans} = 10.9$ Hz, $J_{cis} = 8.2$ Hz, $J_{CH_3} = 6.1$ Hz, $=CHCH_3$), 2.14 (dd, $J_{cis} = 8.2$ Hz, $J_{gem} = 1.4$ Hz, $=CHH$), 1.84 (dd, $J_{trans} = 10.9$ Hz, $J_{gem} = 1.4$ Hz $= CHH$), 1.81 (d, $J = 6.1$ Hz, CH_3); ^{13}C NMR (CD_2Cl_2, 126 Hz) δ 203.9 (s, CO), 203.8 (s, CO), 85.6 (d, $J = 179$ Hz, C_5H_5), 33.6 (d, $J = 154$ Hz, $C{=}CH_2$), 24.0 (q, $J = 126$ Hz, CH_3), 20.9 (t, $J = 154$ Hz, $=CH_2$); IR (hexane) 1975 (s), 1906 (s) cm^{-1}; HRMS calcd for $C_{10}H_{11}O_2Re$ 350.0317, found 350.0320. Anal. Calcd for $C_{10}H_{11}O_2Re$: C, 34.47; H, 2.89. Found: C, 34.42; H, 2.99.

(8) Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc. A* **1971**, 2667. **5** is readily detected by the ^1H NMR of the CH_3 group (δ 2.43 (dt, $J = 7.7$ Hz, $J_{PH} = 1.8$ Hz, $J_{PtH} = 53.4$ Hz)).

(9) Dissociation of alkenes from Re is extremely slow. For example, displacement of the alkene from $Cp(CO)_2Re(CH_2{=}CHCH_2CMe_3)$ required heating at 200 °C with PPh_3 in C_6D_6 for days.[10]

(10) Casey, C. P.; Askham, F. R., unpublished results.

(11) Reaction of $Cp(CO)_2Re(THF)$ with alkenes produces a mixture of alkene complexes, $CpRe(CO)_3$, and other products.

(12) Similar transfer of H and CO between Ir and Re was proposed in the reaction of $Ir(CO)Cl(PPh_3)_2$ with **2**.

(13) Burch, R. R.; Muetterties, E. L.; Teller, R. G.; Williams, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 4257.

(14) Abley, P.; McQuillen, F. J. *J. Chem. Soc., Chem. Commun.* **1969**, 1503.

knowledged. We thank Johnson-Matthey for a generous loan of precious metals.

Supplementary Material Available: Full spectral characterization of $(C_5H_5)(CO)_2Re(CH_2{=}CH_2)$, **6**, **7**, **8**, *cis*-**9**, and *trans*-**9** (2 pages). Ordering information is given on any current masthead page.

Stereoselective Oxidative Additions of a Carbon–Carbon σ-Bond in Tetrafluorocyclopropene to Iridium(I) Complexes

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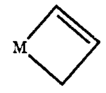
Received July 31, 1989

The stoichiometric and catalytic transition metal promoted reactions of cyclopropenes are of considerable interest and synthetic utility.[1] Opening of the cyclopropene ring by the metal center occurs frequently, to yield putative vinylcarbene intermediates **1** or isomeric metallacyclobutenes **2**. Only two vinylcarbene complexes[2,3] and a single example of a metallacyclobutene complex[4] have actually been isolated from such cyclopropene reactions. The mechanism of ring opening has been unclear, but the recent observation that 3,3-diphenyl-1-cyclopropene reacts with $[Zr(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}1\text{-butene})(PMe_3)]$ to afford a mixture of isomers **3** and **4**, which do not interconvert thermally, has led to the suggestion by Binger[3] that "vinylcarbene complexes...are formed by direct opening of the cyclopropene ring and not via an η^2-cyclopropene intermediate". Here we confirm that the stereoselectivity of cyclopropene ring opening by Ir(I) complexes is indeed consistent with direct activation of a σ-bond by the metal center.

1



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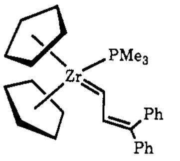

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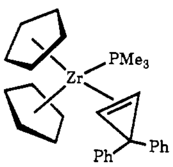

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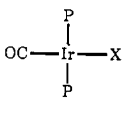
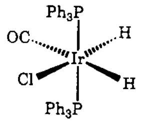


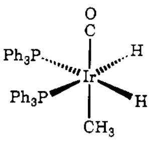
5 a. P = PPh3, X = Cl

b. P = PPh3, X = CH3

c. P = PMe3, X = Cl



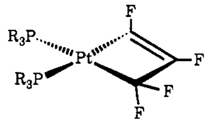
6



7

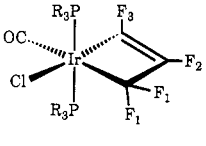
Oxidative addition of the σ-bond of the H_2 molecule to square-planar Ir(I) complexes (**5**) has been thoroughly studied.[5,6] Two stereoselective pathways have been defined for kinetically controlled addition; **5a** reacts to give stereoisomer **6**, while **5b** reacts to give **7**. Similar stereoselectivity is obtained for the addition of the $R_3Si{-}H$ σ-bond to the same Ir(I) substrates, and detailed theoretical rationales for the effect of ancillary ligands on the stereocontrol of these reactions have been published.[5,6]

We have shown previously that formal oxidative addition of tetrafluorocyclopropene to the platinum(0) center in $[Pt(C_2H_4)(PR_3)_2]$ occurs rapidly at −78 °C to afford the platinacyclobutene complexes **8**.[4] Similarly, tetrafluorocyclopropene reacts stereoselectively with **5a** at −78 °C in toluene solution, to yield quantitatively a ca. 1:1 mixture of two isomeric Ir(III) metallacyclobutene complexes. Each isomer exhibits a ^{19}F NMR spectrum containing three resonances of relative intensity 2:1:1 and a ^{31}P NMR spectrum containing a single resonance. The isomers must therefore have structures **9a** and **10a**, each possessing a mirror plane which includes the metallacyclic ring and which relates the phosphine ligands.[7] In contrast, tetrafluorocyclopropene reacts with **5b** to give a quantitative yield of a single isomer, whose ^{19}F NMR spectrum exhibits four equal-intensity resonances and whose ^{31}P NMR spectrum shows two inequivalent phosphorus environments. Accordingly, the structure of this isomer is assigned as **11a**.[7] In contrast to its PPh_3 analogue, the PMe_3 complex **5c** reacts with slightly less stereoselectivity, to give a mixture of **9b** (45%), **10b** (45%), and **11b** (10%).[8] This ratio



8 a. R = Ph

b. R = Me



9 a. R = Ph

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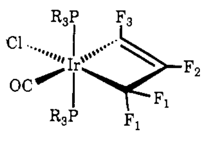
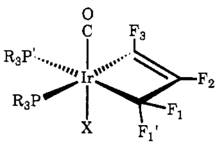


10 a. R = Ph

b. R = Me



11 a. R = Ph; X = Me

b. R = Me; X = Cl

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(1) For a review of the transition-metal chemistry of cyclopropenes, see: Binger, P.; Buch, H. M. In *Topics in Current Chemistry*; Meijere, A., Ed.; Springer-Verlag: Berlin, GDR, 1987; pp 77–151.

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(7) Satisfactory microanalytical results (C, H; ±0.4% of calculated values) were obtained for all complexes. NMR assignments were confirmed by selective $^{19}F\{^{19}F\}$, $^{19}F\{^{31}P\}$, and $^{31}P\{^{19}F\}$ decoupling experiments. **9a**: ^{19}F NMR ($CDCl_3$) (282 MHz; positive chemical shifts upfield from $CFCl_3$) δ 74.1 (m, 2 F_1), 105.4 (m, F_2), 124.9 (m, F_3), $J_{1,2} = 7$, $J_{1,3} = 20$, $J_{2,3} = 15$, $J_{P-F3} = 4$ Hz; $^{31}P\{^1H\}$ NMR ($CDCl_3$) (121 MHz; positive chemical shifts downfield from H_3PO_4) δ 2.1 (m); IR ($CHCl_3$) ν(CO) = 2025 cm^{-1}. **10a**: ^{19}F NMR ($CDCl_3$) δ 86.7 (m, 2 F_1), 106.2 (m, F_3), 112.7 (m, F_2), $J_{1,2} = 5$, $J_{1,3} = 19$, $J_{2,3} = 11$ Hz; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −5.2 (m); IR ($CHCl_3$) ν(CO) = 2057 cm^{-1}. **11a**: ^{19}F NMR ($CDCl_3$) δ 79.7 (m, F_1), 104.2 (m, F_2), 109.3 (m, $F_{1'}$), 118.9 (m, F_3), $J_{1,1'} = 205$, $J_{1,3} = 19$, $J_{1,P'} = 35$, $J_{1,P} = 5$, $J_{1',3} = 20$, $J_{1',P'} = 36$, $J_{1',P} = 3$, $J_{2,3} = 10$, $J_{2,P} = 22$, $J_{2,P'} = 22$, $J_{3,P} = 56$, $J_{3,P'} = 4$ Hz; ^1H NMR ($CDCl_3$) δ 7.5–7.2 (30 H, br m, Ph), 0.34 (3 H, t, $J_{H,P} = 15$ Hz, Me); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −2.1 (m, P′), −6.5 (m, P); IR ($CHCl_3$) ν(CO) = 2031 cm^{-1}.

0002-7863/89/1511-8919$01.50/0