ORGANOMETALLICS

Steric effects in carbon monoxide insertion into manganese-carbon bonds

John D. Cotton, and Ross D. Markwell

Organometallics, **1985**, 4 (5), 937-939• DOI: 10.1021/om00124a024 • Publication Date (Web): 01 May 2002 was shown to contain a bridging hydride and four different phosphorus atoms. An intriguing feature was the observation by ^{31}P NMR of two trans P–P coupling constants ($J_{P_1P_3}$ = 253.9 Hz, $J_{P_2P_4}$ = 274.7 Hz) whereas only one phosphorus is coupled to rhodium (J_{Rh-P_1} = 120.85 Hz). The spectrum was simulated by using the PANIC program[9] (Figure 1). The only possible structure should contain four phosphorus substituents on ruthenium, one part of a bridging phosphido group. This was confirmed by an X-ray crystal structure determination[10] (Figure 2). Selected bond distances and angles are listed in Table I. The four phosphorus are bonded to ruthenium. P(1) bridges the metal–metal bond together with one hydride. The Ru–Rh distance, 2.9413 (8) Å, is consistent with the presence of a hydrido-bridged metal–metal bond (see 2.933 Å for $Pt_2H(Me)_2(dppm)_2^+$). The most interesting feature is the presence of a phenyl group bonded to ruthenium. This can only arise from the cleavage of a P–C bond mediated by ruthenium. Interestingly, such an intermediate has never been isolated in the decomposition of dppm on clusters.[11] Some products of pyrolysis of clusters in the presence of PPh_3 have been shown to contain coordinated phenyl groups.[12] In our case, the reaction occurs at room temperature and is selective. The same structure remains in solution as confirmed by ^{13}C NMR which shows the phenyl group bonded to ruthenium[13] (C–Ru δ 163.7, C_{ortho} 149.3, C_{meta} 94.2, C_{para} 120.0). The mechanism of formation of this complex probably involves an unstable dihydrido methyl intermediate which after elimination of methane leaves a very reactive 16-electron ruthenium moiety. This is stabilized by insertion into a P–C bond of dppm to achieve an 18-electron configuration. We are presently studying the reactivity of this interesting species.

Registry No. 1, 95531-46-7; 2, 95531-47-8; 3, 34216-12-1; 4, 89613-06-9; 5, 95531-48-9; 6, 95531-49-0; 6·0.5 $C_6H_5CH_3$, 95531-50-3; $RhH[P(OMe)_3]_4$, 59400-49-6; $RuH_2(dppm)_2$, 89613-08-1; $[RhCl(COD)]_2$, 12092-47-6; $[IrCl(COD)]_2$, 12112-67-3; $PdCl_2(COD)$, 12107-56-1.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters, complete bond distances and angles, and structure factors (33 pages). Ordering information is given on any current masthead page.

---

(10) Crystal data: $C_{58}H_{57}P_4RhRu\cdot0.5C_6H_5CH_3$: a = 15.985 (3) Å, b = 18.324 (4) Å, c = 19.496 (4) Å, β = 112.2 (2)°, monoclinic, space group C^5_{2h}—$P2_1/c$, Z = 4. Intensity data were recorded in θ–2θ scan mode on a CAD4 diffractometer using Mo Kα radiation. Full-matrix least-squares refinement with 4751 reflections having $I > 4\sigma(I)$ led to final R = 0.034.

(11) Lavigne, G.; Lugan, N.; Bonnet, J. J. *Organometallics* 1982, *1*, 1040–1050.

(12) See for example: Bradford, C. W.; Nyholm, R. S.; Gainsford, G. J.; Guss, J. M.; Ireland, P. R.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1972**, 87–89.

(13) These values are similar to that found for mononuclear phenylruthenium complexes: see, for example: Saunders, D. R.; Stephenson, M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1473–1477.

Steric Effects in Carbon Monoxide Insertion into Manganese–Carbon Bonds

John D. Cotton* and Ross D. Markwell

Chemistry Department, University of Queensland
Brisbane, Australia 4067

Received November 26, 1984

Summary: The reactivity of the manganese–benzyl complexes $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ toward carbon monoxide insertion induced by tertiary phosphines in polar solvents has been studied. The steric influences of the alkyl group, solvent, and the phosphine are discussed.

Earlier we have drawn attention to steric effects in the tertiary phosphine induced insertion of carbon monoxide into transition metal to carbon bonds for series of alkyl complexes, $[(\eta^5\text{-}C_5H_5)(CO)_3MoR]$[1,2] and $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$.[3] We have noted a rate enhancement with increase in the size of the alkyl group, R, in the k_1 step of the reaction schematically represented as eq 1, where L = tertiary phosphine and S = solvent. This step, on strong kinetic and stereochemical grounds,[2–6] is believed to involve a solvent-induced migration of the alkyl group to a carbonyl carbon atom. Interestingly a substantial diminution in k_1 has also been observed for the reaction of diphenylmethylphosphine with $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_3]$ as the effective size of the solvent in a series of α-substituted tetrahydrofurans increases, which is thought to reflect increasing steric hindrance to the coordination of the tetrahydrofuran to molybdenum.[6] We have also detected[2] a large decrease in the rate constant k_2 for $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2Ph]$ and $[(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2Cy]$ systems when the cone angle of the tertiary phosphine,[7] which replaces the solvent molecule in the intermediate acyl in this stage of the reaction, exceeds a critical value. This effect is enhanced in the corresponding (pentamethylcyclopentadienyl)molybdenum benzyl complex and only relatively small ligands, such as dimethylphenylphosphine, react. In the belief that the substantial steric effects may largely be reflecting the influence of the large, nonlabile cyclopentadienyl group, we extended our work to a metal alkyl system which contains only CO ligands and which should be less restricted sterically at the metal center. Specifically, carbon monoxide insertion has been followed, in acetonitrile, tetrahydrofuran, 2-methyltetrahydrofuran, and 2,5-dimethyltetrahydrofuran at 30 °C, for a series of manganese–benzyl complexes, $[(CO)_5Mn(CH_2C_6H_{5-n}X_n)]$, strategically substituted in the aromatic ring, using tertiary phosphines of different cone angles.[10]

$$[\mathrm{(CO)MR}] \underset{k_{-1},\,-\mathrm{S}}{\overset{k_1,\,\mathrm{S}}{\rightleftharpoons}} [\mathrm{SM(COR)}] \underset{k_{-2},\,-\mathrm{L}}{\overset{k_2,\,\mathrm{L}}{\rightleftharpoons}} [\mathrm{LM(COR)}] + \mathrm{S} \tag{1}$$

The effect of the size of the alkyl group was examined by comparing the effect on k_1 of substitution of an alkyl group, for which electronic effects are small,[1,11] in the ortho

---

(1) Cotton, J. D.; Kimlin, H. A.; Markwell, R. D. *J. Organomet. Chem.* **1982**, *232*, C75.

(2) Cotton, J. D.; Markwell, R. D. *Inorg. Chim. Acta* **1982**, *63*, 13.

(3) Cotton, J. D.; Crisp, G. T.; Latif, L. *Inorg. Chim. Acta* **1981**, *47*, 171.

(4) Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 3994.

(5) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101.

(6) Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028.

(7) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(8) Cotton, J. D.; Kimlin, H. A., unpublished data.

(9) Closson, R. D.; Kozikowski, J.; Coffield, T. H. *J. Org. Chem.* **1957**, *22*, 598.

(10) In a typical experiment, a solution of 0.023 g (0.08 mmol) of $[(CO)_5MnCH_2Ph]$ and 0.20 g (0.76 mmol) of triphenylphosphine in 10 ml of acetonitrile was degassed in a Schlenk tube in a constant temperature bath (30.0 ± 0.1 °C). Periodically, a sample was withdrawn, by syringe, through a serum cap and reaction followed by monitoring the disappearance of the highest energy CO stretching vibration (2111 cm^{-1}) of the starting material. Reaction was followed for around 3 half-lives and, at this high relative concentration of tertiary phosphine, was effectively first order in $[(CO)_5MnCH_2Ph]$. The reaction was repeated for different phosphine concentrations which tyically ranged from 0.025 to 0.2 M. A plot of the reciprocal of the observed first-order rate constant, i.e., $1/k_{obsd}$ vs. $1/[L]$, where L = tertiary phosphine, was linear and enabled the calculation of k_1 and k_{-1}/k_2, based on the overall rate expression,[4] $k_{obsd} = k_1k_2[L]/(k_{-1} + k_{-2}[L])$, appropriate for polar solvents. Uncertainty parameters vary with the system, but a general guide is ±5% for k_1 and ±10% for the ratio k_{-1}/k_2. In this concentration range, the direct reaction (k_3 path) of tertiary phosphine with $[(CO)_5MnR]$ was insignificant.

0276-7333/85/2304-0937$01.50/0

Table I. Rate Constants for Reaction of Ph_3P with $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ in Acetonitrile at 30 °C

substnt X_n	$10^5k_1/s^{-1}$	substnt X_n	$10^5k_1/s^{-1}$
H	30	2,4,6-Me_3	123
o-Me	25	2,4,6-*i*-Pr_3	412
p-Me	43	Me_5	180

position(s) of the benzyl moiety, with that for para substitution of the same ligand, in reactions with triphenylphosphine in acetonitrile (Table I). The *o*-methyl manganese complex reacted significantly more slowly than the *p*-methyl, which is the reverse of our observation for the $[(\eta^5\text{-}C_5H_5)(CO)_3MoR]$ system[2] (*o*-Me, $k_1 = 7.3 \times 10^{-4}$ s^{-1}; *p*-Me, $k_1 = 3.9 \times 10^{-4}$ s^{-1}). A more striking difference is seen for the isopropyl substituent: while the *o*-isopropyl molybdenum complex reacts about 40 times faster than the para, the rates are comparable in the manganese system ($k_1 = 3.1 \times 10^{-4}$ s^{-1} at 22 °C).[12] For molybdenum, di-ortho substitution leads either to modest rate enhancement over the singly substituted complex ($k_1 = 8.5 \times 10^{-4}$ s^{-1} for 2,4,6-trimethylbenzyl) or to complete inhibition (for 2,4,6-triisopropylbenzyl). For the corresponding manganese compounds, a large increase in k_1 is observed in each case. The (pentamethylbenzyl)manganese compound reacts more readily than the 2,4,6-trimethylbenzyl compound.

Our explanation of the data for the cyclopentadienylmolybdenum system was that enhancement in k_1 with increasing size of the alkyl group reflected the relief of congestion in the transition state in which the metal to alkyl carbon bond is partially broken and lengthened. However, we postulated that inhibition, such as that observed with very large groups such as 2,4,6-triisopropylbenzyl on molybdenum, could occur if the steric interactions were so severe as effectively to lock the alkyl group in position and prevent the migration of the benzylic carbon atom. The results for the manganese system appear contradictory on these grounds. The unexpectedly high reactivity of the di-ortho manganese compounds compared with their molybdenum counterparts can, however, be interpreted in terms of significantly reduced steric effects at the metal center which are, in this case, insufficient to prevent alkyl migration. The high k_1 value observed for the (pentamethylbenzyl)manganese compound compared with the 2,4,6-trimethylbenzyl system probably results from the increased steric effect of the *o*-methyl groups produced by repulsive interactions with the *m*-methyl substituents, but mild electronic enhancement could also arise.[10] The lower reactivity, on manganese, of the *o*-methyl compared with the *p*-methyl system is not predicted either by our steric model or electronically. The result may indicate that there is a lower limit for steric interaction below which the favorable energy terms arising from the lengthening of the metal–carbon bond in the k_1 transition state are insignificant and in fact dominated by another factor. The reactivity model would then include the concept of a steric "window" at the metal center outside of which reactivity toward carbon monoxide insertion decreases.

Table II. Rate Constants for Reaction of Ph_3P with $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ in Substituted Tetrahydrofurans at 30 °C

substnt X_n	solvent	$10^5k_1/s^{-1}$
H	THF	6.7
H	2-MeTHF	4.1
H	2,5-Me_2THF	2.8
o-Me	THF	5.8
o-Me	2-MeTHF	3.3
o-Me	2,5-Me_2THF	3.7
2,4,6-Me_3	THF	19.2
2,4,6-Me_3	2-MeTHF	10.9
2,4,6-Me_3	2,5-Me_2THF	5.1

Table III. Rate Constants for Reaction of Tertiary Phosphines with $[(CO)_5MnCH_2Ph]$ in Acetonitrile at 30 °C

tertiary phosphine	cone angle/deg	10^5k_1/ s^{-1}	$10^3k_{-1}/k_2$/ mol L^{-1}
PMe_2Ph	122	30.3	1.4
P-*n*-Bu_3	132	31.4	1.8
$PMePh_2$	136	30.6	2.3
$PEtPh_2$	140	29.6	2.6
PPh_3	145	29.0	5.3
P-*i*-$PrPh_2$	150	29.7	5.2
P-*t*-$BuPh_2$	157	31.8	21
$P(C_6H_{11})_3$	170	29.4	33

Large steric influences on the reactivity of $[(CO)_5MnCH_2Ph]$ with triphenylphosphine have also been observed over the three solvents, tetrahydrofuran (THF), 2-methyltetrahydrofuran (2-MeTHF), and 2,5-dimethyltetrahydrofuran (2,5-Me_2THF) which have similar polarity but steadily increasing effective size.[6] The results (Table II) are generally compatible with those of Wax and Bergman, for the reactions of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_3]$ with diphenylmethylphosphine in these solvents,[6] with k_1 decreasing with increasing solvent size, and can again be interpreted on the basis of decreasing effective nucleophilicity of the solvent. However, significant differences between the manganese and cyclopentadienylmolybdenum systems exist. For $[(CO)_5MnCH_2Ph]$, the ratio of the fastest to the slowest k_1 value is 2.4 whereas for $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_3]$ it is 34, an observation which again points to the generally lower level of steric congestion for manganese.

The analysis of the rate constants observed in these solvents for benzyl-, (*o*-methylbenzyl)-, and (2,4,6-trimethylbenzyl)manganese systems is complicated by the interplay of the steric effects of the solvent and the alkyl group. In the solvents tetrahydrofuran and 2-methyltetrahydrofuran, there is a decrease in k_1 in going from the benzyl to the *o*-methylbenzyl compound and then a larger increase to 2,4,6-trimethylbenzyl. The trend is the same as that discussed earlier for acetonitrile. However, for 2,5-dimethyltetrahydrofuran, a steady increase in k_1 is seen which suggests that the steric influence of the single *o*-methyl substituent is now substantially increased to the extent that the system now finds itself in the "window" for steric enhancement. The relative increase from benzyl to 2,4,6-trimethylbenzyl becomes less as the size of the solvent increases, the ratio being 3.8 for tetrahydrofuran and 2.4 for 2,5-dimethyltetrahydrofuran. This suggests either some degree of enhancement in k_1 for the benzyl compound for 2,5-dimethyltetrahydrofuran or rate inhibition for the 2,4,6-trimethylbenzyl system in the same solvent.

Steric influences are also strongly expressed in the ratio of rate constants, k_{-1}/k_2, which steadily decreases with increasing phosphine cone angle for the reactions of $[CO)_5MnCH_2Ph]$ in acetonitrile (Table III). Because the k_1 values obtained for these reactions are, within experimental uncertainty, independent of the phosphine, it is reasonable to expect a similar constancy in k_{-1} and the

---

(11) Cotton, J. D.; Crisp, G. T.; Daly, V. A. *Inorg. Chim. Acta* **1981**, *47*, 165.

(12) This experiment was conducted on a mixture of the *o*- and *p*-isopropylbenzyl complexes by monitoring the methylene proton resonances of starting material (2.3 ppm) and product (4.0 ppm) at 22 °C on a Bruker CXP 300 NMR spectrometer.

trend in k_{-1}/k_2 should thus be influenced solely by k_2, the second-order rate constant for the replacement of a solvent molecule in the intermediate by tertiary phosphine. The trend is the same as that observed previously for $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2Ph]$ in acetonitrile and with $[(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2Cy]$ in dimethyl sulfoxide.[2] In keeping with the lower steric congestion in the manganese complex, the decrease in k_2 is less abrupt and reactivity extends to higher cone angles (e.g., tricyclohexylphosphine (170°) reacts with $[(CO)_5MnCH_2Ph]$ at 30 °C, but with neither of the cyclopentadienylmetal compounds).

Registry No. THF, 109-99-9; 2-MeTHF, 96-47-9; 2,5-Me_2THF, 1003-38-9; $[(CO)_5MnCH_2C_6H_5]$, 14049-86-6; $[(CO)_5MnCH_2C_6H_4$-*o*-Me], 95891-55-7; $[(CO)_5MnCH_2C_6H_4$-*p*-Me], 95891-56-8; $[(CO)_5MnCH_2C_6H_2$-2,4,6-$Me_3]$, 95891-57-9; $[(CO)_5MnCH_2C_6H_2$-2,4,6-(*i*-Pr)$_3]$, 95891-58-0; $[(CO)_5MnCH_2C_6Me_5]$, 56800-76-1; Ph_3P, 603-35-0; PMe_2Ph, 672-66-2; P-*n*-Bu_3, 998-40-3; $PMePh_2$, 1486-28-8; $PEtPh_2$, 607-01-2; P-*i*-$PrPh_2$, 6372-40-3; P-*t*-$BuPh_2$, 6002-34-2; $P(C_6H_{11})_3$, 2622-14-2; CO, 630-08-0.

Preparation and Chemistry of Novel Platinum(II) Amide Complexes Containing β-Hydrogens[†]

Henry E. Bryndza,* William C. Fultz, and Wilson Tam*

Central Research and Development Department
E. I. du Pont de Nemours and Company
Experimental Station, Wilmington, Delaware 19898

Received February 8, 1985

Summary: Synthesis of new platinum(II) amide complexes has been accomplished both by metathesis of $L_2PtR(Cl)$ (L_2 = DPPE = 1,2-bis(diphenylphosphino)ethane, R = CH_3, CH_3, C_6H_5, $CH_2C_6H_5$; L_2 = DMPE = 1,2-bis(dimethylphosphino)ethane, R = CH_3), with $LiNCH_3(C_6H_5)$ and by exchange of free amine with the analogous methoxide complexes. $(DPPE)PtCH_3[N(CH_2C_6H_5)(H)]$, prepared from $(DPPE)PtCH_3(Cl)$ and $LiN(CH_2C_6H_5)(H)$, reacts with CO to give $(DPPE)PtCH_3[C(O)N(CH_2C_6H_5)(H)]$. $(DMPE)PtCH_3[NCH_3(C_6H_5)]$ crystallizes from THF/hexane in space group $P2_1/n$ with cell dimensions $a = 6.2790$ (8) Å, $c = 16.894$ (2) Å, and $\beta = 96.47$ (1)° with $Z = 4$. The favorable equilibrium for the displacement of methanol by *N*-methylaniline suggests the metal–nitrogen bond is much less prone to dissociation of amide than are metal–oxygen bonds to dissociation of methoxide and requires the Pt–OCH_3 homolytic bond strength be 16 kcal/mol stronger than the Pt–$NCH_3(C_6H_5)$ bond. Reaction of $(DPPE)PtCH_3(NCH_3(C_6H_5))$ with methyl iodide and acetyl chloride shows these amide complexes react as nucleophiles despite their inability to dissociate free amide.

Late-transition-metal amide complexes have been postulated in several amine based routes to organic nitrogen-containing chemicals.[1] For example, the reaction of amines with carbon monoxide and oxygen to give carbamates is a potential route to important insecticides; it may involve late metal amides[1a,b] and would, if successfully developed, preclude the need to prepare and handle dangerous isocyanates and phosgene. Despite this potential, very little is known about the chemistry of late-transition-metal amide complexes primarily because relatively few such compounds are known and those possessing β-hydrogen atoms are particularly difficult to isolate.[2] We wish to report the synthesis of Pt(II) alkyl amide complexes and several reactions that demonstrate the reactivity of the platinum–nitrogen bond.

Reaction of $L_2PtR(Cl)$ (L_2 = DPPE = 1,2-bis(diphenylphosphino)ethane, R = CH_3, C_6H_5, $CH_2C_6H_5$; L_2 = DMPE = 1,2-bis(dimethylphosphino)ethane, R = CH_3[3]) with 1 equiv of $LiN(CH_3)(C_6H_5)$ in THF results in the formation of platinum(II) amide complexes (eq 1). Isolation is accomplished by solvent removal followed by extraction with benzene or CH_2Cl_2. Concentration of the solutions followed by precipitation with hexane allows isolation of air-sensitive yellow platinum(II) amide complexes in greater than 65% yields. Similarly, the reaction of $LiN(CH_2C_6H_5)(H)$ with $(DPPE)PtCH_3(Cl)$ yields $(DPPE)Pt(CH_3)[N(CH_2C_6H_5)(H)]$.[4] Using $LiN(CH_3)_2$ in place of $LiN(CH_3)C_6H_5$ at low temperature resulted in the formation of unstable dimethylamide complexes which decompose above 0 °C. These species have not been isolated in pure form.

$$L_2PtRCl + LiNCH_3(C_6H_5) \rightarrow L_2PtR[NCH_3(C_6H_5)] \quad (1)$$

$(DPPE)Pt(CH_3)[N(CH_2C_6H_5)(H)]$ reacts with 3 atm of CO at 25 °C to give $(DPPE)Pt(CH_3)[C(O)NCH_2C_6H_5(H)]$ in 80% yield. Similarly, the reaction of $(DPPE)Pt(CH_3)(N(CH_3)_2)$ (generated in situ) with CO leads to $(DPPE)Pt(CH_3)[C(O)N(CH_3)_2]$ in 76% isolated yield. Although the reactions of CO with the Pt–$N(CH_3)(C_6H_5)$ complexes reported in this paper appear to give analogous insertion products, we have not been able to isolate them because deinsertion in these cases appears to be facile. There is no evidence for insertion into the Pt–C bond. These are the first examples of CO insertion into late transition metal–nitrogen bonds and these transformations

---

[†] Contribution No. 3606.

[1] (a) Fukuoka, S.; Chono, M.; Kohno, M. *J. Org. Chem.* **1984**, *49*, 1458. (b) Fukuoka, S.; Chono, M.; Kohno, M. *J. Chem. Soc., Chem. Commun.* **1984**, 399. (c) Moir, M.; Chiba, K., Ban, Y. *J. Org. Chem.* **1978**, *43*, 1684. (d) Alper, H.; Urso, F. *J. Am. Chem. Soc.* **1983**, *105*, 6737.

[2] (a) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1983**, *2*, 682. (b) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1983**, *2*, 355. (c) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J.; Secco, A. S.; Trotter, J. *Organometallics* **1982**, *1*, 918. (d) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Ellis Horwood, Chichester, 1980. (e) Beck, W.; Bauder, M. *Chem. Ber.* **1970**, *103*, 583.

[3] $(DMPE)PtCH_3(NC_6H_5(CH_3))$ crystallizes from THF/hexane in space group $P2_1/n$ with cell dimensions $a = 6.2790$ (8) Å, $b = 16.111$ (2) Å, $c = 16.894$ (2) Å, and $\beta = 96.47(1)$ with $Z = 4$. In this structure the trigonal plane of nitrogen is 68° out of the coordination plane of platinum. Additional information is available as supplementary material.

[4] Proton NMR of complexes in THF-d_8 unless otherwise noted. $(DPPE)Pt(CH_3)[NCH_3(C_6H_5)]$: δ 7.80 (m, 4 H), 7.69 (m, 4 H), 7.48 (m, 6 H), 7.30 (m, 6 H), 6.69 (t, J = 8 Hz, 2 H), 6.48 (d, J = 8 Hz, 2 H), 5.91 (t, J = 7 Hz, 1 H), 5.37 (d, J = 3.4 Hz, J_{Pt} = 34 Hz, 3 H), 2.3 (m, 4 H), 0.52 (dd, J = 4.7, 7.8 Hz, J_{Pt} = 64 Hz, 3 H). $(DMPE)Pt(CH_3)[NCH_3(C_6H_5)]$: δ 6.72 (t, J = 7.5 Hz, 2 H), 6.40 (d, J = 7.5 Hz, 2 H), 5.90 (t, J = 7.6 Hz, 1 H), 2.8 (d, J = 3 Hz, J_{Pt} = 32 Hz, 3 H), 1.8 + 1.5 (m, m, 4 H), 1.55 (d, J = 10 Hz, J_{Pt} = 37 Hz, 6 H), 1.30 (d, J = 9 Hz, J_{Pt} = 17 Hz, 6 H), 0.35 (dd, J = 8, 5 Hz, J_{Pt} = 62 Hz). $(DPPE)PtPh(NPhCH_3)$: δ 7.7 (m, 4 H), 7.6 (m, 4 H), 7.4 (m, 12 H), 7.03 (m, 2 H), 6.5 (m, 5 H), 6.45 (d, J = 8 Hz, 2 H), 5.79 (t, J = 7 Hz, 1 H), 2.5 (d, J = 3 Hz, J_{Pt} = 36 Hz, 3 H), 2.35 (m, 4 H). $(DPPE)Pt(CH_2Ph)(NPhCH_3)$: δ 7.77 (m, 4 H), 7.50 (br s, 8 H), 7.25 (m, 6 H), 6.60 (m, 4 H), 6.40 (d, J = 6 Hz, 2 H), 5.90 (t, J = 7 Hz, 1 H), 2.74 (dd, J = 10, 6 Hz, J_{Pt} = 90 Hz, 2 H), 2.31 (d, J = 4 Hz, J_{Pt} = 31 Hz, 3 H), 2.3 + 2.1 (m, 4 H). $(DPPE)Pt(CH_3)[NH(CH_2Ph)]$: δ 8.0 (m, 4 H), 7.7 (m, 4 H), 7.4 (m, 12 H), 7.14 (d, J = 6 Hz, 2 H), 7.04 (t, J = 6 Hz, 2 H), 6.94 (t, J = 6 Hz, 1 H), 4.28 (dd, J = 4, 8 Hz, J_{Pt} = 33 Hz, 2 H), 0.78 (t, J = 7 Hz, J_{Pt} = 69 Hz, 1 H), 0.32 (dd, J = 5, 7 Hz, J_{Pt} = 65 Hz, 3 H). $(DPPE)Pt(CH_3)[C(O)N(CH_3)_2]\cdot THF$: ^1H NMR (δ, CD_2Cl_2) 0.54 (dd, J = 6.9, 8.2, J_{Pt} = 72 Hz, 3 H), 2.69 (s, J_{Pt} = 5.4 Hz, 3 H), 2.72 (s, 3 H), 8.1 (m) + 7.8 (m) + 7.5 (m) (20 H), and 2.55 (m) + 2.15 (m) (4 H) along with THF resonances. $(DPPE)PtCH_3[C(O)NCH_2Ph(H)]$: δ 5.68 (t, J = 5.4 Hz, 1 H), 4.25 (d, J = 5.7 Hz, 2 H, with unresolved Pt satellite), 2.3 (m, 4 H), 0.74 (dd, J = 7, 8 Hz, J_{Pt} = 72 Hz, 3 H) and aromatic protons. Elemental analyses and other spectral data on these complexes are available as supplementary material.

0276-7333/85/2304-0939$01.50/0