which in turn was prepared by reacting methyl formate-*d* with chlorotris(trimethylphosphine)(cyclooctene)iridium(I).[7] NMR spectra were recorded at ambient probe temperature by using a Nicolet/GE QE-300 instrument. ^{1}H NMR spectra for all compounds are reported in Table I.

In a typical exchange reaction, compound **1a** (0.03 g) in CD_3CN solution was treated with 2 equiv of Ph_4AsCl. The NMR spectrum, run within 30 min of mixing, showed 85% conversion of the iodo formyl compound **1a** to the known[7] chloro formyl compound **1b**, with no decomposition products detectable. Addition of further amounts of Ph_4AsCl drove the reaction essentially to completion. The ^{1}H NMR spectrum of the reaction solution was identical (hydride, formyl, $P(CH_3)_3$) with the ^{1}H NMR spectrum of an authentic sample of compound **1b** prepared by the literature route.[7] The equilibrium constant for the reaction **1a** + $(C_6H_5)_4AsCl \rightleftharpoons$ **1b** + $(C_6H_5)_4AsI$ is 4.1 ± 0.1 at 20 °C in CD_3CN.

For a quantitative determination of the rate of PMe_3 exchange, the ^{1}H NMR spectrum of a CD_3CN solution of compound **1a** (initially 0.087 M) and PMe_3 (initially 0.173 M) was monitored. The pseudo-first-order rate constant for the reaction **1a** → **1d** was 0.053 ± 0.001 min^{-1}; $t_{1/2}$ = 13 min at 20 °C.

In our attempt to force the ^{12}C–^{13}C interconversion of compound **1e**-^{13}*C*, a sapphire NMR tube[17] containing [^{13}*C*]formyl compound **1a**-^{13}C in CD_3CN was pressurized to 25 atm with ^{12}CO. After 24 h at room temperature the solution contained approximately equal amounts of compound **1e**-^{13}*CHO* and *mer*-$[IrH_2(^{13}CO)(PMe_3)_3]I$. No **1e**-^{12}*CHO* could be detected. The NMR tube was then heated to 80 °C. After 24 h *mer*-$[IrH_2(^{12}CO)(PMe_3)_3]I$ was the only detectable compound present.

(17) Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388–391.

Ligand Effects and Nucleophilic Addition to (η^3-Allyl)palladium Complexes. A Carbon-13 Nuclear Magnetic Resonance Study[1]

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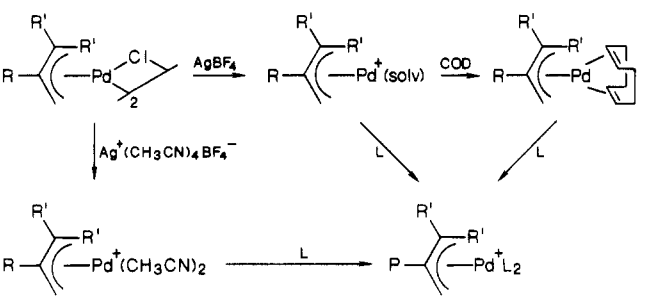
With the use of acceptor ligands such as phosphines, large downfield ^{13}C shifts may be induced selectively at the more substituted terminus of an unsymmetric (η^3-allyl)palladium system. Bidentate ligands with one acceptor and one donor function may induce even greater relative downfield shifts at the more substituted terminus. The observed downfield chemical shifts follow closely the anticipated acceptor properties of the ligands, suggesting that there may be a relation between ^{13}C NMR shifts and relative charge at the η^3-allyl termini.

Nucleophilic addition to η^3-allyl systems has been extensively applied to selective organic synthesis, in particular after the development by Trost and associates of catalytic reactions starting with allylic acetates.[2] One important problem with these reactions is to control the regiochemistry. For instance, the reaction of **64** (L^1 = PPh_3, L^2 = Cl^-) with the anion of dimethyl malonate gives a mixture of the two possible regioisomers. However, when more sterically demanding nucleophiles such as the anion of benzenesulfonyl acetate are used,[2c] the less substituted terminus of the η^3-allyl system reacts preferentially.

In a recent study of the reactions of (η^3-geranyl)palladium complexes, it was observed that ligands such as triphenylphosphine induced reactivity at the more substituted η^3-allyl terminus[3] while bipyridine promoted reaction at the less substituted terminus.[3a] This result can be interpreted as a correlation between acceptor properties of the ligands and relative reactivity at the more substituted η^3-allyl terminus. Selective reaction at the more substituted η^3-allyl terminus has been observed before[2c,4,5] but explained in terms of relative stability of the products[2c,4a] or by the intermediacy of a σ-complex.[5] However, another explanation is that acceptor ligands such as triphenylphosphine selectively induce positive charge at the more substituted η^3-allyl terminus. In fact, Trost and his associates have recently presented results from molybde-

Scheme I



(1) Presented in part at XIIth International Conference on Organometallic Chemistry, Vienna, 1985.

(2) (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (b) Trost, B. M.; Verhoeven, T. R. *Compr. Organomet. Chem.* **1982**, *8*, 799. (c) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730.

(3) (a) Åkermark, B.; Vitagliano, A. *Organometallics*, **1985**, *4*, 1275. (b) Åkermark, B.; Hansson, S.; Krakenberger, B.; Vitagliano, A.; Zetterberg, K. *Organometallics* **1984**, *3*, 679.

(4) (a) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416. (b) Adams, R. D.; Chodosh, D. F.; Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 2570.

(5) Takahashi, U.; Tsukiyama, K.; Sakai, S.; Ishii, Y. *Tetrahedron Lett.* **1970**, 1913.

0276-7333/87/2306-0620$01.50/0

num- and tungsten-catalyzed η^3-allyl reactions that may be explained in terms of charge control.[6] A simple method for monitoring relative charges within an η^3-allyl unit would therefore be of interest, and the exploratory study of the η^3-geranyl system[3] suggested that ^{13}C NMR shifts might be useful. We therefore decided to study in detail the influence of the ligands on the ^{13}C shifts of three representative η^3-allyl systems: the (η^3-2-methylpropenyl) (**1–12**), the (η^3-butenyl) (**13–33**), and the (η^3-3-methylbutenyl) systems (**34–75**).

Preparation and Characterization of the Complexes

All the complexes were prepared from the well-known bridged chloride complexes **3**, **17**, and **40**. The monomeric, neutral complexes of the type (η^3-allyl)Pd(L)Cl (L = PR_3, $P(OR)_3$, CH_3NC) were prepared by splitting the chloride bridge with the appropriate ligand. The cationic complexes (η^3-allyl)PdL_2^+ were prepared by three similar methods (Scheme I). In the simplest procedure, the chloride was removed by reaction with $AgBF_4$, and the appropriate ligands were then added.

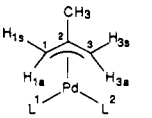
Alternatively, 1,5-cyclooctadiene was added immediately after the treatment with $AgBF_4$. In this way, stable, isolable cationic complexes, with a ligand that could readily be displaced by other ligands, were obtained. Finally, in an essentially equivalent procedure, the chloride complexes were treated with $Ag(CH_3CN)_4BF_4$ to give the cationic bis(acetonitrile) complexes which likewise could be isolated and kept in the pure, crystalline state and then converted to other complexes by treatment with the appropriate ligands.

The three procedures were also used for preparing cationic complexes with unsymmetrical bidentate ligands. The mixed cationic complexes (η^3-allyl)PdL^1L^{2+}, finally, where L^1 = PPh_3 or $P(OPh)_3$ and L^2 = CH_3CN, pyridine, CH_3NC, etc, were made by treating the phosphine–chloride complexes (η^3-allyl)Pd(PR_3)Cl with $AgBF_4$ and then with the appropriate second ligand. Due to moderate stability or difficult crystallization and problems with the exact stoichiometry of the crystalline complexes, many of the complexes were only prepared in solution and never isolated, but a complete characterization by ^1H and/or ^{13}C NMR was generally possible.

The addition of two different ligands L^1 and L^2 to the η^3-butenyl- and η^3-3-methyl-2-butenyl complexes would generally be expected to yield a pair of cis and trans isomers. In most cases, either L^1 or L^2 was PR_3. Since phosphorus atoms earlier have been shown (i) to have a larger trans than cis coupling constant both to carbon and the protons on this carbon and (ii) to cause a strong downfield shift at the trans carbon,[7] the stereochemistry of these unsymmetrical complexes was readily determined.

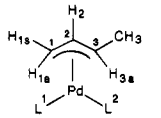
For example, in the bis(triphenylphosphine) complex **51**, H_{1s} (J_P = 7.2 Hz) and H_{1a} (J_P = 9.6 Hz) couple only with the trans phosphine ligand, and in the mixed phosphine–pyridine complex **63**, no phosphorus–proton coupling is observed. These data are in accord with a structure where the phosphine ligand is trans to the more substituted allyl terminus C-3. Similarly, the phosphorus–carbon trans coupling is much larger than the cis coupling, and in **63** only coupling to C-3 (23.8 Hz) is observed. These observations are in complete accord with an early observation by Shaw et al. on the chloride–phosphine complex **9**.[7] The usefulness of the phosphorus coupling is also nicely demonstrated by the couplings in the two isomeric 1-(dimethylamino)-2-(diphenylphosphino)ethane complexes **60** and **72**. In **60**, the phosphorus coupling is 26.5 Hz to C-3 and 3.4 Hz to C-1, and no coupling for H_{1a} and H_{1s} is observed. In **72** the phosphorus coupling is 5.0 Hz to C-3 and 28.3 Hz to C-1 and 6.2 Hz and 9.2 Hz to H_{1s} and H_{1a}, respectively. Accordingly, the structure with the phosphorus atom trans to C-3 was assigned to **60**, and that with the phosphorus atom trans to C-1 was assigned to **72**.

Table I. ^{13}C NMR Shifts for the η^3-Allyl Unit of the (η^3-2-Methylpropenyl)palladium(II) Complexes



		shifts, ppm		
		C_1	C_2	C_3
1	L^1, L^2 = TMEDA	59.9	134.9	59.9
2	L^1 = L^2 = py	61.35	135.9	61.35
3	L^1 = L^2 = Cl^- (bridged)	61.9	127.0	61.9
4	L^1 = L^2 = CH_2CN	63.2	134.7	63.2
5	L^1, L^2 = diphos	70.4	137.7	70.4
6	L^1, L^2 = COD	75.9	141.3	75.9
7	L^1 = L^2 = PPh_3	78.55	138.2	78.55
8	L^1 = PBu_3, L^2 = Cl^-	51.5	130.9	77.6
9	L^1 = PPh_3, L^2 = Cl^-	61.6	132.85	78.0
10	L^1 = PPh_3, L^2 = py	58.8	137.5	80.0
11	L^1, L^2 = $Ph_2PCH_2CH_2NMe_2$	51.4	137.2	80.7
12	L^1 = PPh_3, L^2 = CH_3CN	60.0	137.2	81.2

Table II. ^{13}C NMR Shifts for the η^3-Allyl Unit of (η^3-Butenyl)palladium(II) Complexes



		shifts, ppm			shift diff,
		C_1	C_2	C_3	$C_3 - C_1$
13	L^1 = L^2 = CH_3NH_2	56.1	116.45	74.9	19
14	L^1, L^2 = TMEDA	59.3	118.4	75.4	16
15	L^1 = L^2 = pyr	58.3	118.9	79.4	21
16	L^1 = L^2 = $(CH_3)_2CO$	57.05	114.2	79.5	22
17	L^1 = L^2 = Cl^- (bridged)	58.3	111.4	81.5	23
18	L^1 = L^2 = CH_3CN	59.8	117.2	83.6	24
19	L^1, L^2 = diphos	65.6	122.8	92.0	26
20	L^1 = L^2 = $AsPh_3$	71.9	120.6	98.1	26
21	L^1, L^2 = COD	71.4	124.5	98.3	27
22	L^1 = L^2 = PPh_3	73.6	122.1	101.5	28
23	L^1 = L^2 = $P(OPh)_3$	68.05	123.2	102.0	34
24	L^1 = PPh_3, L^2 = CN^-	61.25	120.3	90.95	30
25	L^1 = PBu_3, L^2 = Cl^-	46.1	115.4	98.75	53
26	L^1, L^2 = $Ph_2PCH_2CH_2NMe_2$	48.1	119.9	99.4	51
27	L^1 = PPh_3, L^2 = Cl^-	56.3	116.95	99.6	43
28	L^1 = $P(OEt)_3$, L^2 = Cl^-	50.55	117.6	101.15	51
29	L^1 = $P(OPh)_3$, L^2 = Cl^-	51.8	117.25	101.5	50
30	L^1 = PPh_3, L^2 = py	54.2	120.35	101.5	47
31	L^1 = $P(OPh)_3$, L^2 = py	52.4	121.4	104.1	52
32	L^1 = PPh_3, L^2 = CH_3CN	55.0	119.55	105.4	50
33	L^1, L^2 = $Me_2NCH_2CH_2PPh_2$	77.6	124.0	71.2	−6

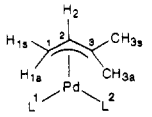
Results and Discussion

Selected ^{13}C and ^1H NMR data are listed in the Tables I–IV. Since the ultimate goal of our work is to effect selective reactivity at the more substituted terminus of η^3-allyl systems, the unsymmetric η^3-butenyl and η^3-3-methylbutenyl systems were more extensively studied than the symmetric η^3-2-methylpropenyl system. In Tables I–IV the compounds are arranged according to the shift at C-3, the low-field terminus. For clarity, the symmetrically substituted (L^1 = L^2) complexes of the 2-methylpropenyl

(6) (a) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1983**, *105*, 3343. (b) Trost, B. M.; Hung, M.-H. *Ibid.* **1983**, *105*, 7757.

(7) Mann, B. E.; Pietropaolo, R.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1971**, 790 and earlier references.

Table III. ^{13}C NMR Shifts for the η^3-Allyl Unit of Symmetrically Substituted (η^3-3-Methyl-2-butenyl)palladium(II) Complexes



		shifts, ppm			shift diff,
		C_1	C_2	C_3	$C_3 - C_1$
34	$L^1 = L^2 = CH_3NH_2$	53.2	110.4	87.9	35
35	L^1, L^2 = TMEDA	56.15	112.1	88.45	32
36	$L^1 = L^2 = PhCH_2NH_2$	52.9	109.9	89.1	36
37	$L^1 = L^2 = Ph_3PO$	50.75	104.75	91.7	41
38	$L^1 = L^2$ = py	55.6	112.7	92.2	37
39	$L^1 = L^2 = (CH_3)_2CO$	54.2	108.5	94.2	40
40	$L^1 = L^2 = Cl^-$ (bridged)	55.8	106.4	95.05	39
41	$L^1 = L^2 = CH_3CN$	56.8	111.1	98.8	42
42	$L^1 = L^2 = Ph_3PS$	59.2	108.3	105.7	46
43	$L^1, L^2 = PhS(CH_2)_2SPh$	63.6	114.7	108.3	45
44	$L^1, L^2 = Ph_2P(CH_2)_2PPh_2$	61.0	115.45	108.7	48
45	$L^1 = L^2 = CH_3NC$	59.35	114.6	108.95	50
46	$L^1 = L^2 = PEt_3$	56.7	112.8	112.79	56
47	$L^1 = L^2 = PBu_3$	57.0	112.75	112.8	56
48	L^1, L^2 = COD	67.3	118.0	114.3	47
49	$L^1 = L^2 = P(OMe)_3$	59.1	115.7	115.7	57
50	$L^1 = L^2 = AsPh_3$	65.1	113.05	117.1	52
51	$L^1 = L^2 = Pph_3$	65.65	113.75	119.4	54
52	$L^1 = L^2 = P(4\text{-}ClPh)_3$	67.5	114.8	121.2	54
53	$L^1 = L^2 = P(OPh)_3$	60.2	114.65	124.4	64

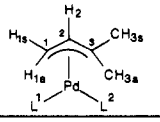
and the butenyl systems are arranged in an array separated from the unsymmetrically substituted complexes ($L^1 \neq L^2$) in Tables I and II.

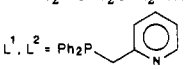
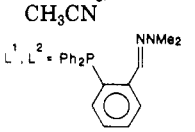
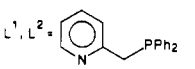
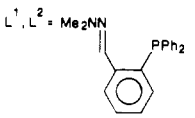
The trends in the effects of the ligands become clear from the results for the complexes **1–7**, **13–23**, and **34–53**, which contain two identical ligands (Tables I–III). As the ligands go from pure donors, such as TMEDA and chloride, to ligands which could also have acceptor character, such as phosphines[8a] and phosphites, the ^{13}C shifts at the η^3-allyl termini C-1 and C-3 are displaced downfield. For instance, the shifts at C-1 and C-3 of the TMEDA complex **1** are ca. 60 ppm and for the corresponding triphenylphosphine complex **7** are ca. 79 ppm. Also the shifts at the central carbon C-2 depend on the ligands, but the trends are less clear, perhaps because the highest occupied allyl orbital, which should interact most strongly with acceptors, has a node at C-2.

The extensive data for the η^3-3-methylbutenyl system show that the downfield shift is fairly gradual and smooth as the ligands go from pure donors to fair acceptors (Table III). The shift at C-3, the more substituted position, is more strongly affected than that at C-1. The C-3 shifts are found at relatively high field, ca. 88 ppm, when the ligands are simple amines as in the complexes **34–36**. Although pyridine, acetone, and acetonitrile are unsaturated, they induce only moderate downfield shifts, down to ca. 99 ppm for the acetonitrile complex **41**. This result is in sharp contrast to isocyanide and COD which cause big downfield shifts, the value for the COD complex **48** being 114 ppm. The reason is perhaps that these ligands π-bond more efficiently to the metal. Sulfur atoms in the ligands appear to introduce acceptor character. Triphenylphosphine sulfide, in contrast to triphenylphosphine oxide, induces a fair downfield shift at C-3 (106 ppm). Also 1,2-bis(phenylthio)ethane acts as an acceptor, and the shift for complex **43**, 108 ppm, is essentially equal to that of the 1,2-bis(diphenylphosphino)ethane complex **44**. Most other phosphines and phosphites cause bigger shifts, the biggest,

(8) (a) Ikuta, S.; Kebarle, P.; Bancroft, G. M.; Chan, T.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 5899. (b) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953.

Table IV. ^{13}C NMR Shifts for the η^3-Allyl unit of Unsymmetrically Substituted (η^3-3-Methylbutenyl)Palladium(II) Complexes



		shifts, ppm			shift diff,
		C_1	C_2	C_3	$C_3 - C_1$
54	$L^1 = PPh_3, L^2 = CN^-$	56.9	113.6	107.4	51
55	$L^1 = CH_3NC, L^2 = Cl^-$	50.4	109.8	108.8	58
56	$L^1, L^2 = Ph_2PCH_2CH_2NH_2$	46.5	111.6	112.65	66
57	$L^1 = PBu_3, L^2 = Cl^-$	42.3	108.4	114.5	72
58	$L^1 = PPh_3, L^2 = I^-$	57.9	111.4	115.0	57
59	$L^1 = PPh_3, L^2 = SCN^-$	≈56 (br)	110.9	115.2	59
60	$L^1, L^2 = Ph_2PCH_2CH_2NMe_2$	43.6	111.2	115.2	72
61		45.3	111.7	115.3	70
62	$L^1 = PCy_3, L^1 = Cl^-$	41.9	107.7	115.5	74
63	$L^1 = PPh_3, L^2$ = py	50.0	112.6	116.2	66
64	$L^1 = PPh_3, L^2 = Cl^-$	52.2	110.2	116.5	64
65	$L^1 = PPh_3, L^2 = CH_3NC$	59.1	114.0	117.5	58
66	$L^1 = P(OEt)_3, L^2 = Cl^-$	46.3	110.3	118.1	72
67	$L^1 = P(OMe)_3, L^2 = Cl^-$	46.3	110.4	119.0	73
68	$L^1 = P(OPh)_3, L^2 = Cl^-$	47.5	110.05	120.05	73
69	$L^1 = P(OPh)_3, L^2$ = py	47.55	113.0	120.35	73
70	$L^1 = PPh_3, L^2 = CH_3CN$	50.8	112.2	122.7	72
71		44.7	111.6	123.0	78
72	$L^1, L^2 = Me_2NCH_2CH_2PPh_2$	73.5	118.6	85.6	
73		73.3	118.8	86.2	
74		78.2	118.6	86.5	
75	$L^1, L^2 = H_2NCH_2CH_2PPh_2$	67.8	116.5	88.3	

124 ppm, exhibited by the triphenyl phosphite complex **53**. The relative order of the downfield shifts, triphenyl phosphite > triphenylphosphine > acetonitrile > pyridine > amine, agrees well with the relative acceptor powers that have been derived from IR and NMR studies of substituted carbonyl complexes.[8b,9] Also the order among the phosphorous ligands, triphenyl phosphite > tris(4-chlorphenyl)phosphine > triphenylphosphine > tributylphosphine, is in agreement with earlier results for carbonyl complexes.[8b]

For the η^3-butenyl and the η^3-3-methylbutenyl systems, there is a shift difference between the two η^3-allyl termini. When the ligands are donors, this shift difference corresponds fairly closely to that expected upon substitution of one or two hydrogens at one terminus by methyl groups. However, the difference increases with the acceptor power of the ligands. For example, the C-3 to C-1 shift difference is 32 ppm for the TMEDA complex **35** but is increased to 64 ppm when TMEDA is replaced by triphenyl phosphite (complex **53**). The effect of the methyl groups at C-3 is reminiscent of their effect on electrophilic addition to olefins, where positive charge in the intermediate is

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preferentially induced at the more substituted terminus.

Earlier studies of the mixed phosphine–chloride complex **9** and some related complexes have shown that a considerable shift difference between the two η^3-allyl termini may be observed when the two ligands are different. This effect is also demonstrated by the shifts for the mixed pyridine–phosphine complex **10**. The shift at C-1, which is trans to the pyridine ligand, is ca. 59 ppm, close to the value 61 ppm observed for the bis(pyridine) complex **2**. Similarly the shift at C-3, which is trans to phosphine, is ca. 80 ppm, as compared to 79 ppm for the bis(phosphine) complex **7**. The ^{13}C shifts at the η^3-allyl termini are thus determined mainly by the trans ligand. This effect can be used to increase further the shift difference between C-3 and C-1 of η^3-butenyl- and η^3-3-methylbutenyl complexes, since in these systems an acceptor ligand will preferentially occupy the position trans to the more substituted terminus C-3. The data for a series of η^3-3-methylbutenyl complexes with mixed donor–acceptor ligands (Table IV) very nicely illustrate this effect, and a maximum shift difference of 79 ppm is observed for the complex **71**.

The data in Table IV also permit an evaluation of the effect of the formal charge on the shifts. This correlation is of interest for relating charge and reactivity of η^3-allyl complexes, and we have earlier suggested that the formal charge may not necessarily correlate with reactivity.[3b] A comparison of the C-3 shifts for a series of η^3-3-methylbutenyl complexes, which all have triphenylphosphine as one ligand, is particularly instructive. For the neutral complexes, the shift goes from 107 ppm for the cyanide complex **54** to 116 ppm for the chloride complex **64**, the iodide and isothiocyanide complexes falling in between. When chloride is replaced by the neutral ligand pyridine, the shift is unchanged at 116 ppm for the complex **63**. When the second ligand is an acceptor, the shift for the cationic complexes is moderate, 117 and 119 ppm for the isocyanide complex **65** and the triphenylphosphine complex **51**, respectively. The biggest downfield shift, 123 ppm, is observed for both the cationic complex **71** and, somewhat surprisingly, the acetonitrile–phosphine complex **70**. These results suggest that there is no fundamental difference between neutral and cationic complexes and that the donor–acceptor properties of the ligands may be more important than their formal charge.

The effects of the ligands on the shifts of the η^3-allyl termini, in particular the correspondence between acceptor power and downfield NMR shifts, in combination with the effect of the methyl substituents indicate that there may be a correlation also between downfield shifts and relative positive charge. Such a correlation would be very useful for predicting reactivity but meets with several potential problems. NMR shifts would be expected to be sensitive to hybridization. It has even been suggested that the relative downfield shift at C-3 in the phosphine–chloride complex **9** is due to differences in double-bond character in the C-3 to C-2 and C-2 to C-1 bonds.[7] In support, an X-ray crystal structure was cited[10] which appears to be in error.[11] Also, the comparison with the shifts for the bridged chloride complex **3** and the bis(phosphine) complex **7** indicates that other effects are more important than hybridization.

Another serious problem with attempts to correlate charge and ^{13}C NMR shifts is that the shifts result from a complex interplay between shielding and deshielding effects (for extensive discussions, see ref 12). Fortunately, it appears that fairly good correlations may be observed for groups of closely related unsaturated compounds,[12] and it seems possible that simple (η^3-allyl)palladium complexes constitute such a group. If this conclusion is correct, the present NMR study suggests that acceptor ligands will increase both the reactivity of η^3-allyl systems and the preference for reaction at the more substituted terminus of an (η^3-allyl)palladium system. Experiments designed to test this hypothesis are in progress.

Experimental Section

The NMR spectra were recorded on a Bruker WP 200 instrument, operating at 200 MHz for ^1H and at 50.3 MHz for ^{13}C. With the exception of compounds **8**, **16**, **25**, **28**, **39**, **57**, **62**, **66**, and **67**, which were generated in situ, and a few others used as crude samples owing to difficult crystallization, the spectra were recorded for freshly recrystallized samples dissolved in $CDCl_3$ to a concentration of 0.05–0.10 M for ^1H and 0.15–0.30 M for ^{13}C spectra. The shifts are expressed in δ (ppm) relative to Me_4Si as internal standard. Homo- and heteronuclear coupling constants in the ^1H spectra could generally be determined by a first-order analysis, using double irradiation techniques when necessary to confirm the assignments. In some cases resolution enhancement was used to resolve partially overlapping lines. The digital resolution (Hz/data point) was 0.12 Hz for ^1H and 0.6 Hz for ^{13}C spectra.

Because of the straightforward method used in the preparation of the complexes, ^1H and ^{13}C NMR data were generally assumed sufficient for a full characterization of the compounds, but a few selected elemental analyses were also done.

When coordinating impurities could be excluded, the ^1H NMR spectra of the cationic complexes were those expected for a nondynamic η^3-allyl system,[13-16] and the assignments for the proton resonances were straightforward. In order to save space, the proton couplings of the η^3-allyl units are not reported individually. For the η^3-2-methylpropenyl complexes, $0 < J_{gem} < 2$ Hz, $J_{1a,3a} \simeq 0$ Hz, and $0 < J_{1s,3s} < 3$ Hz, for the η^3-butenyl system, $0 < J_{1s,1a} < 2$ Hz, $6.7 < J_{1s,2} < 7.7$ Hz, $11.6 < J_{1a,2} < 13.6$ Hz, and $11.5 < J_{23} < 13.0$ Hz, and for the η^3-3-methylbutenyl system, $1.3 < J_{1s,1a} < 3.0$ Hz, $7.4 < J_{1s,2} < 8.2$ Hz, and $12.5 < J_{1a,2} < 14.3$ Hz. Also, only relevant ^1H resonances are reported. Complex multiplets arising from the ancillary ligand(s) are generally omitted.

The coordination of the ancillary ligands was shown by the changes in shifts for both ligands and the η^3-allyl unit in ^1H as well as ^{13}C NMR and/or by the increase in the multiplicity of the ligand resonances due to the asymmetry of the allyl group. For the phosphorous ligands, additional proof was given by the observed ^{31}P couplings.

The assignments in the ^{13}C spectra are consistent with those reported for chloride-bridged complexes and some other η^3-allyl complexes.[13,17,18] By the use of selective proton decoupling, the

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^{13}C assignments could generally be ascertained.

Ligands. 1-Amino-2-(diphenylphosphino)ethane[19] and 1-(dimethylamino)-2-(diphenylphosphino)ethane[23] were both prepared according to literature procedures by reaction between the aminoethyl bromide and lithium diphenylphosphide.

2-[(Diphenylphosphino)methyl]pyridine. All steps of the following procedure were performed under a nitrogen atmosphere, and all solvents were carefully deaerated to avoid oxidation of the product.

n-Butyllithium (25 mmol, 15.63 mL, 1.6 M in hexane) was added over a period of 20 min to 2-picoline (2.33 g, 25 mmol) in 20 mL of dry THF at −20 °C. After being stirred for 1 h, the mixture was slowly aded to a solution of $ClPPh_2$ (5.5 g, 25 mmol) in 25 mL of dry THF at −60 °C over a period of 30 min. The temperature was allowed to rise to 0 °C over 45 min. After the mixture was cooled to −25 °C, 50 mL of water was added over 10 min. The mixture was stirred for 30 min. The product was obtained by first extracting with 0.3 N HCl(aq), then neutralizing with a $NaHCO_3$ solution, and extracting with dichloromethane. The solvent and any unreacted 2-picoline were removed under vacuum (oil pump) during the course of 1 h. The yield of crude product was 75% (>90% purity). No further attempts to purify the product were made, because of its easy oxidation to the corresponding phosphine oxide and of the earlier report[20,22] that vacuum distillation resulted in decomposition: ^1H NMR δ 8.50–6.80 (m, C_5H_4N), 8.00–7.00 (m, PC_6H_5), 3.64 (s, CH_2); ^{13}C NMR δ 157.93 (d, J = 7.3 Hz, Pic-2), 149.19 (Pic-6), 138.04 (d, J = 14.9 Hz, Ph-1), 136.01 (Pic-4), 132.76 (d, J = 19.1 Hz, Ph-2), 128.62 (Ph-4), 128.30 (d, J = 6.2 Hz, Ph-3), 123.55 (d, J = 6.1 Hz, Pic-3), 120.91 (Pic-5), 38.74 (d, J = 16.2 Hz, CH_2) (Ph = phenyl, Pic = 2-picolyl).

Note: In solution, stirring with air leads to rapid oxidation to the phosphine oxide. In fact, the procedure for the preparation of the phosphine, which has been published, gives the phosphine oxide, as also shown by the NMR data presented in that publication.[20]

[2-(*N*,*N*-Dimethylhydrazonomethyl)phenyl]diphenylphosphine (2-(Diphenylphosphino)benzaldehyde *N*,*N*-Dimethylhydrazone).[25] 2-(Diphenylphosphino)benzaldehyde[22] (2.00 g, 6.9 mmol) and 0.413 g (6.9 mmol) of *N*,*N*-dimethylhydrazine were dissolved in 100 mL of absolute ethanol, and a trace of toluenesulfonic acid was added. The solution was refluxed for 5 h and then cooled at −20 °C overnight, giving a colorless crystalline precipitate. A second crop was obtained by concentrating the mother liquid and cooling at −20 °C (yield 78%). The compound was characterized through its complex **71**.

Allyl Complexes. Bis(μ-chloro)bis[(1,2,3-η)-2-methyl-2-propenyl]dipalladium (3) was prepared from palladium(0) and 2-methylpropenyl chloride according to a published procedure:[21] ^{13}C NMR δ 127.01 (C-2), 61.89 (C-1, C-3), 22.82 (CH_3).

Bis(acetonitrile)[(1,2,3-η)-2-methyl-2-propenyl]palladium Tetrafluoroborate (4). The dimeric chloride complex **3** (2 g, 5.1 mmol) was dissolved in 10 mL of dichloromethane, and after the mixture was cooled to 0 °C, a solution of $Ag(CH_3CN)_4BF_4$ (3.66 g, 10.2 mmol) in 10 mL of dichloromethane was added. After the solution was stirred for 5 min, the precipitated silver chloride was removed by filtration and the filtrate concentrated to a small volume. Addition of ether and vigorous shaking gave **4** (3.37 g, 90%): ^{13}C NMR δ 134.71 (C-2), 122.32 (CN), 63.19 (C-1, C-3), 22.75 (CH_3), 2.76 (CH_3CN); ^1H NMR δ 4.13 (s, H_{1s}, H_{3s}), 3.02 (s, H_{1a}, H_{3a}), 2.41 (s, CH_3CN), 2.15 (s, CH_3). The spectrum of the hexafluorophosphate salt in acetone has been reported.[17]

(Tetramethylethylenediamine)[(1,2,3-η)-2-methyl-2-propenyl]palladium Tetrafluoroborate (1). The acetonitrile complex **4** (0.5 g, 1.5 mmol) was dissolved in 5 mL of dichloromethane, the solution cooled to −20 °C, and 3.0 mmol of tetramethylethylenediamine (TMEDA) was added. The solvent was then evaporated at a temperature below 0 °C and the crude product washed with ether. Recrystallization from dichloromethane–ether gave the complex **1** (0.49 g, 90%): mp 205–206 °C dec; ^{13}C NMR δ 134.89 (C-2), 60.64 (CH_2N), 59.90 (C-1, C-3), 52.33, 51.50 (CH_3N), 23.61 (CH_3); ^1H NMR δ 3.52 (s, H_{1s}, H_{3s}), 2.92 (s, H_{1a}, H_{3a}), 2.96, 2.82 (s, CH_3N), 2.13 (s, CH_3).

Bis(pyridine)[(1,2,3-η)-2-methyl-2-propenyl]palladium tetrafluoroborate (2) and [(1,2,5,6-η)-1,5-cyclooctadiene][(1,2,3-η)-2-methyl-2-propenyl]palladium tetrafluoroborate (6) were prepared by the same procedure.

[1,2-Bis(diphenylphosphino)ethane][(1,2,3-η)-2-methyl-2-propenyl]palladium tetrafluoroborate (5) and bis(triphenylphosphine)[(1,2,3-η)-2-methyl-2-propenyl]palladium tetrafluoroborate (7) were prepared by the same procedure except that only the stoichiometric amount of ligand was added. The yields were in all cases in the range 85–95%.

2: ^{13}C NMR δ 151.96 (py-2), 138.94 (py-4), 135.86 (C-2), 126.19 (py-3), 61.35 (C-1, C-3), 23.43 (CH_3); ^1H NMR δ 3.83 (s, br, H_{1s}, H_{3s}), 3.28 (s, br, H_{1a}, H_{3a}), 2.27 (CH_3) (py = pyridine). **5**: mp 92–99 °C; ^{13}C NMR δ 137.74 (t, J = 6.0 Hz, C-2), 132.54, 132.46 (t, J = 6.3 Hz, Ph-2, Ph-2′), 131.96 (s, Ph-4), 129.99, 129.45 (quint, J = 22.3 Hz, Ph-1, Ph-1′), 129.77, 129.67 (t, J = 5.4 Hz, Ph-3, Ph-3′), 70.40 (quint, J = 17 Hz, C-1, C-3), 27.33 (t, J = 23 Hz, CH_2), 24.32 (CH_3); ^1H NMR δ 4.63 (m, H_{1s}, H_{3s}), 3.28 (m, H_{1a}, H_{3a}), 1.95 (s, CH_3). **6**: mp 210–217 °C dec; ^{13}C NMR δ 141.34 (C-2), 113.78, 112.02 (C=C), 75.89 (C-1, C-3), 29.36 (CH_2), 23.06 (CH_3); ^1H NMR δ 4.78 (s, H_{1s}, H_{3s}), 3.70 (s, H_{1a}, H_{3a}), 2.06 (s, CH_3). **7**: mp 219–222 °C dec; ^{13}C NMR δ 138.17 (t, J = 5.2 Hz, C-2), 133.57 (t, J = 6.7 Hz, Ph-2), 131.24 (t, J = 22.3 Hz, Ph-1), 131.10 (s, Ph-4), 129.06 (t, J = 5.2 Hz, Ph-3), 78.55 (t, J = 14.9 Hz, C-1, C-3), 23.54 (CH_3); ^1H NMR δ 3.7 (m, H_{1s}, H_{3s}, H_{1a}, H_{3a}), 1.90 (CH_3).

Chloro(tributylphosphine)[(1,2,3-η)-2-methyl-2-propenyl]palladium (8) was prepared in situ in $CDCl_3$ solution by addition of the stoichiometric amount of tributylphosphine to the bridged chloride complex **3**. The solution was then filtered and used directly for ^{13}C NMR measurements: ^{13}C NMR δ 130.92 (d, J = 4.0 Hz, C-2), 77.57 (d, J = 32 Hz, C-3), 51.51 (br s, C-1), 26.50 (s, Bu-2), 24.28 (d, J = 24.4 Hz, Bu-1), 23.85 (d, J = 16.1 Hz, Bu-3), 23.35 (CH_3), 13.59 (Bu-4).

Chloro(triphenylphosphine)[(1,2,3-η)-2-methyl-2-propenyl]palladium (9) was prepared by reacting the bridged chloride complex **3** with the stoichiometric amount of triphenylphosphine in CH_2Cl_2 at room temperature. After evaporation of the solvent, the product was recrystallized from CH_2Cl_2–diethyl ether to give the pure product **9** in about 85% yield: ^{13}C NMR δ 133.81 (d, J = 13.0 Hz, Ph-2), 132.85 (d, J = 5.0 Hz, C-2), 132.34 (d, J = 41.5 Hz, Ph-1), 130.26 (Ph-4), 128.41 (d, J = 10.0 Hz, Ph-3), 77.98 (d, J = 31.8 Hz, C-3), 61.56 (C-1), 23.21 (CH_3).

(Pyridine)(triphenylphosphine)[(1,2,3-η)-2-methyl-2-propenyl]palladium Tetrafluoroborate (10). The triphenylphosphine complex **9** (1 g, 2.17 mmol) in 5 mL of CH_2Cl_2 was reacted at room temperature with $Ag(CH_3CN)_4BF_4$ (0.78 g, 2.17 mmol) in 5 mL of CH_2Cl_2. The precipitated AgCl was removed by filtration, and pyridine (0.17 g, 2.17 mmol) was added at 0 °C to the filtered solution. Evaporation at 0 °C, washing with a small amount of diethyl ether, and crystallization from diethyl ether–CH_2Cl_2 gave **10** (1.1 g, 85%): mp 155–158 °C dec; ^{13}C NMR δ 152.24 (py-2), 138.28 (py-4), 137.51 (d, J = 5.2 Hz, C-2), 133.42 (d, J = 13.4 Hz, Ph-2), 131.06 (Ph-4), 130.01 (d, J = 43.2 Hz, Ph-1), 129.12 (d, J = 10.4 Hz, Ph-3), 125.91 (py-3), 80.03 (d, J = 28.3 Hz, C-3), 58.82 (C-1), 23.43 (CH_3); ^1H NMR δ 4.59 (dd, J_P = 5.6 Hz, H_{3s}), 4.02 (d, J_P = 9.3 Hz, H_{3a}), 3.36 (m, J_P = 2 Hz, H_{1s}), 3.12 (br s, H_{1a}), 2.13 (CH_3). Anal. Calcd for $C_{27}H_{27}BF_4NPPd$: C, 55.0; H, 4.6; N, 2.4; P, 5.25. Found: C, 55.2; H, 4.6; N, 2.3; P, 5.5.

In solution, **10** disproportionates to a mixture of **10**, the bis(pyridine) complex **2**, and the bis(phosphine) complex **7**.

(Acetonitrile)(triphenylphosphine)[(1,2,3-η)-2-methyl-2-propenyl]palladium tetrafluoroborate (12) was prepared the same way as complex **10**: ^{13}C NMR δ 137.18 (d, J = 4.5 Hz, C-2), 133.47 (d, J = 13.4 Hz, Ph-2), 131.38 (d, J = 2.2 Hz, Ph-4), 130.13 (d, J = 43.9 Hz, Ph-1), 129.20 (d, J = 10.4 Hz, Ph-3), 81.16 (d, J = 26.8 Hz, C-3), 59.99 (C-1), 23.14 (CH_3), 2.65 (CH_3CN); ^1H

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(24) At room temperature, no phosphorous coupling was observed, presumably due to rapid ligand exchange.
(25) Personal communication from Dr. Claudo Pellecchia.

NMR δ 5.00 (dd, J_P = 5.7 Hz, H_{3s}), 3.84 (d, J_P = 9.2 Hz, H_{3a}), 3.32 (m, J_P = 2.5 Hz, H_{1s}), 2.93 (d, H_{1a}), 2.20 (CH_3), 2.06 (CH_3CN).

[1-(Dimethylamino)-2-(diphenylphosphino)ethane][(1,2,3-η)-2-methyl-2-propenyl]palladium tetrafluoroborate (11) was prepared the same way as the 1,2-bis(diphenylphosphino)ethane (diphos) complex **5**: mp 181–182 °C dec; ^{13}C NMR δ 137.22 (d, J = 4.9 Hz, C-2), 132.67 (d, J = 13.3 Hz, Ph-2), 132.51 (d, J = 13.8 Hz, Ph-2'), 131.73 (Ph-4), 129.57 (d, J = 10.8 Hz, Ph-3), 129.52 (d, J = 11.0 Hz, Ph-3'), 129.49 (d, J = 46.0 Hz, Ph-1), 128.99 (d, J = 46.0 Hz, Ph-1'), 80.70 (d, J = 30.0 Hz, C-3), 61.61 (d, J = 6.9 Hz, CH_2N), 52.35 (CH_3N), 51.40 (d, J = 2.6 Hz, C-1), 29.27 (d, J = 26.8 Hz, CH_2P), 23.81 (CH_3); ^1H NMR δ 4.62 (dd, J_P = 5.1 Hz, H_{3a}), 3.82 (d, J_P = 9.3 Hz, H_{3a}), 3.80, 3.75 (CH_3N), 3.67 (m, J_P = 2.0 Hz, H_{1s}), 2.75 (H_{1a}) (partly hidden), 2.06 (CH_3). Anal. Calcd for $C_{20}H_{27}BF_4NPPd$: C, 47.5; H, 5.4; N, 2.8. Found: C, 47.6; H, 5.5; N, 2.7.

Bis(methylamine)[(1,2,3-η)-2-butenyl]palladium tetrafluoroborate (13) was prepared as a crude oil from the bis(acetonitrile) complex **18** by adding an excess of $MeNH_2$ to a dichloromethane solution at 0 °C and evaporating the solvent in vacuo: ^{13}C NMR δ 116.45 (C-2), 74.93 (C-3), 56.12 (C-1), 33.63, 31.10 (br, CH_3N), 16.70 (CH_3).

(Tetramethylethylenediamine)[(1,2,3-η)-2-butenyl]palladium tetrafluoroborate (14) was prepared by the procedure used for the 2-propenyl complex **1**: mp 162–163 °C dec; ^{13}C NMR δ 118.40 (C-2), 75.42 (C-3), 61.01, 60.08 (CH_2N), 59.26 (C-1), 52.18, 51.21, 50.36, 49.02 (CH_3N), 16.63 (CH_3); ^1H NMR δ 5.46 (dt, H_2), 3.74 (m, H_{3a}), 3.63 (d, H_{1s}), 3.00 (d, H_{1a}), 2.94, 2.90, 2.78, 2.61 (s, CH_3N), 1.36 (d, CH_3).

Bis(pyridine)[(1,2,3-η)-2-butenyl]palladium tetrafluoroborate (15) was prepared the same way as the bis(pyridine) complex **2**: mp 91–92 °C; ^{13}C NMR δ 151.63 (py-2), 138.73 (py-4), 126.16 (py-3), 118.92 (C-2), 79.37 (C-3), 58.34 (C-1), 16.96 (CH_3); ^1H NMR δ 5.70 (dt, H_2), 4.19 (m, H_{3a}), 3.82 (d, H_{1s}), 3.17 (d, H_{1a}), 1.11 (d, CH_3).

Bis(acetone)[(1,2,3-η)-2-butenyl]palladium tetrafluoroborate (16) was prepared in situ by adding anhydrous $AgBF_4$ (1 mol/mol of Pd) and acetone (2.2 mol/mol of Pd) to a solution of the chloride-bridged dimer **17** in $CDCl_3$ and filtering the precipitated silver chloride: ^{13}C NMR 213.75 (C=O), 114.21 (C-2), 79.52 (C-3), 57.05 (C-1), 31.64 (CH_3C=O), 17.67 (CH_3).

Bis(μ-chloro)bis[(1,2,3-η)-2-butenyl]dipalladium (17) was prepared from 1-chloro-2-butene by a published procedure:[21] ^{13}C NMR δ 111.44 (C-2), 81.48 (C-3), 58.33 (C-1), 18.07 (CH_3).

Bis(acetonitrile)[(1,2,3-η)-2-butenyl]palladium tetrafluoroborate (18) was prepared the same way as the analogous 2-methylpropenyl coimplex **4**: ^{13}C NMR δ 121.81 (C≡N), 117.23 (C-2), 83.63 (C-3), 59.82 (C-1), 17.93 (CH_3), 2.58 (CH_3CN); ^1H NMR δ 5.50 (dt, H_2), 4.12 (m, H_{3a}), 4.11 (d, H_{1s}), 2.96 (d, H_{1a}), 2.35 (s, CH_3CN), 1.44 (d, CH_3).

[1,2-Bis(diphenylphosphino)ethane][(1,2,3-η)-2-butenyl]palladium tetrafluoroborate (19), bis(triphenylarsine)[(1,2,3-η)-2-butenyl]palladium tetrafluoroborate (20), [(1,2,5,6-η)-1,5-cyclooctadiene][(1,2,3-η)-2-butenyl]palladium tetrafluoroborate (21), bis(triphenylphosphine)[(1,2,3-η)-2-butenyl]palladium tetrafluoroborate (22), and bis(triphenyl phosphite)[(1,2,3-η)-2-butenyl]palladium tetrafluoroborate (23) were all prepared from the acetonitrile complex **18** as described for the diphos complex **5**, except that 2 equiv of ligand were used for the cyclooctadiene complex **21**. **19**: mp 147–148 °C dec; ^{13}C NMR δ 132.78, 132.75, 132.53, 132.33 (d, J = 12.4–13.2 Hz, Ph-2), 132.07, 131.82, 131.80, 131.50 (d, J = 2.3–2.5 Hz, Ph-4), 130.09, 129.97, 127.78, 127.74 (dd, J = 40.5–41.5, 2 Hz, Ph-1), 129.85, 129.64, 129.60, 129.60 (d, J = 10.4–10.6 Hz, Ph-3), 122.76 (t, J = 6.5 Hz, C-2), 92.00 (dd, J = 27.3, 6.5 Hz, C-3), 65.56 (dd, J = 28.0, 5.4 Hz, C-1), 28.22, 27.31 (dd, J = 31.4, 14.4 Hz, CH_2P), 18.11 (d, J = 3.3 Hz, CH_3); ^1H NMR δ 5.70 (dt, H_2), 4.58 (m, J_P = 6.0, 1.5 Hz, H_{1a}), 4.36 (m, J_P = 7.8 Hz, H_{3a}), 3.14 (m, J_P = 2.5, 9.8 Hz, H_{1a}), 1.70 (ddd, J_P = 9.5, 8.3 Hz, CH_3). **20**: mp 221–222 °C dec; ^{13}C NMR δ 133.36, 132.19 (Ph-1), 133.26, 133.04 (Ph-2), 130.54, 130.51 (Ph-4), 129.41, 129.31 (Ph-3), 120.61 (C-2), 98.09 (C-3), 71.88 (C-1), 17.87 (CH_3); ^1H NMR δ 5.78 (dt, H_2), 4.79 (m, H_{3a}), 3.99 (dd, H_{1s}), 3.63 (d, H_{1a}), 1.21 (d, CH_3). **21**: mp 195–197 °C dec; ^{13}C NMR δ 124.48 (C-2), 118.74, 114.77, 113.65, 112.08 (C=C), 98.33 (C-3), 71.38 (C-1), 29.56 (2 C), 29.02, 28.49 (CH_2), 18.40 (CH_3); ^1H NMR δ 6.26, 6.13, 5.52 (m, 4 H, HC=C), 5.98 (dt, H_2), 4.89 (m, H_{3a}), 4.70 (d, H_{1s}), 3.61 (d, H_{1a}), 1.79 (d, CH_3). **22**: ^{13}C NMR δ 133.94, 133.73 (dd, J = 12.5, 2.0 Hz, Ph-2), 131.39, 130.22 (dd, J = 33.5, 9.0 Hz, Ph-1), 131.06, 130.98 (d, J = 2.0 Hz, Ph-4), 129.08, 128.98 (dd, J = 8.5, 1.5 Hz, Ph-3), 122.08 (t, J = 6 Hz, C-2), 101.54 (dd, J = 21.5, 8.0 Hz, C-3), 73.56 (dd, J = 21.5, 7.5 Hz, C-1), 17.04 (CH_3); ^1H NMR δ 5.76 (dt, H_2), 4.48 (m, J_P = 8.0 Hz, H_{3a}), 3.53 (t, J_P = 6.0 Hz, H_{1s}), 3.43 (t, J_P = 9.0 Hz, H_{1a}), 1.04 (ddd, J_P = 9.7, 7.6 Hz, CH_3). **23**: mp 156–157 °C; ^{13}C NMR δ 149.90, 149.74 (d, J = 6.0 Hz, Ph-1), 130.3 (Ph-3), 126.28, 126.14 (d, J = 1.0 Hz, Ph-4), 123.24 (t, J = 11.0 Hz, C-2), 120.64, 120.10 (d, J = 6.0 Hz, Ph-2), 101.96 (dd, J = 36.6, 7.5 Hz, C-3), 68.05 (dd, J = 36.8, 5.2 Hz, C-1), 18.31 (dd, J = 6.0, 2.4 Hz, CH_3); ^1H NMR δ 5.10 (ddt, J_P = 2.0 Hz, H_2), 4.09 (m, J_P = 15.5, 2.0 Hz, H_{3a}), 3.89 (m, J_P = 10.8, 2.0 Hz, H_{1s}), 2.39 (t, J_P = 15.0 Hz, H_{1a}), 1.54 (ddd, J_P = 17.6, 11.4 Hz, CH_3).

Cyano(triphenylphosphine)[(1,2,3-η)-2-butenyl]palladium (24). A solution of the chloride complex **27** (1.0 g, 2.18 mmol) in 10 mL of CH_2Cl_2 was shaken with NaCN (0.11 g, 2.18 mmol) in 5 mL of water for 5 min. After separation in the usual way and drying with $MgSO_4$, the organic phase was concentrated to about 1 mL and diethyl ether was added. Compound **24** crystallized as colorless needles in about 90% yield: mp 115–120 °C dec; ^{13}C NMR δ 141.03 (CN), 133.79 (d, J = 13.2 Hz, Ph-2), 132.78 (d, J = 41.3 Hz, Ph-1), 130.54 (Ph-4), 128.66 (d, J = 10.3 Hz, Ph-3), 120.30 (C-2),[24] 90.95 (C-3), 61.25 (C-1), 18.86 (CH_3); ^1H NMR δ 5.35 (dt, H_2), 4.29 (m, H_{3a}), 3.07 (d, H_{1s}), 2.50 (d, H_{1a}), 2.11 (d, CH_3). The analogous complex from the propenyl system has been described.[15]

Chloro(tributylphosphine)[(1,2,3-η)-2-butenyl]palladium (25) was prepared by addition of tributylphosphine to the dimeric chloride complex **17** by the procedure described for the butylphosphine complex **8**: ^{13}C NMR δ 115.44 (d, J = 4.7 Hz, C-2), 98.75 (d, J = 27.4 Hz, C-3), 46.06 (d, J = 1.8 Hz, C-1), 26.48 (Bu-2), 24.93 (d, J = 23.2 Hz, Bu-1), 24.29 (d, J = 13.3 Hz, Bu-3), 17.19 (d, J = 4.3 Hz, CH_3), 13.69 (Bu-4).

(*SP*-4-3)-[1-(Dimethylamino)-2-(diphenylphosphino)ethane][(1,2,3-η)-2-butenyl]palladium tetrafluoroborate (26) was prepared by the procedure used for the diphos complex **5**: mp 132–133 °C; ^{13}C NMR δ 132.89 (d, J = 13.5 Hz, Ph-2), 131.82 (d, J = 2.5 Hz, Ph-4), 129.69 (d, J = 10.5 Hz, Ph-3), 119.92 (d, J = 5.5 Hz, C-2), 99.41 (d, J = 28.0 Hz, C-3), 61.95 (d, J = 7.5 Hz, CH_2N), 51.16, 50.14 (CH_3N), 48.12 (d, J = 3.5 Hz, C-1), 28.98 (d, J = 26.5 Hz, CH_2P), 17.40 (d, J = 3.5 Hz, CH_3); ^1H NMR δ 5.55 (dt, H_2), 4.65 (m, J_P = 9.0 Hz, H_{3a}), 3.66 (dd, H_{1s}), 3.00, 2.77 (s, CH_3N), 2.71 (H_{1a}), 1.87 (dd, J_P = 9.4 Hz, CH_3).

In solution, partial isomerization to **33** takes place (**26**:**33** = 5:3). **33**: ^{13}C NMR 133.23, 132.79 (d, J = 13.5 Hz, Ph-2), 132.10, 131.76 (d, J = 2.5 Hz, Ph-4), 129.89, 129.66 (d, J = 10.5 Hz, Ph-3), 128.46, 128.24 (d, J = 43.5 Hz, Ph-1), 124.04 (d, J = 5.5 Hz, C-2), 77.60 (d, J = 27.5 Hz, C-1), 71.19 (d, J = 4.5 Hz, C-3), 61.68 (d, J = 7.0 Hz, CH_2N), 53.31, 52.76 (CH_3N), 30.53 (d, J = 26.0 Hz, CH_2P), 18.60 (CH_3); ^1H NMR δ 5.77 (ddd, H_2), 4.56 (dd, J_P = 6.4 Hz, H_{1s}), 3.88 (m, H_{3a}), 3.76 (dd, J_P = 9.4 Hz, H_{1a}), 3.04, 2.97 (s, CH_3N), 1.26 (dd, J_P = 8,6 Hz, CH_3).

Chloro(triphenylphosphine)[(1,2,3-η)-2-butenyl]palladium (27) and chloro(triphenyl phosphite)[(1,2,3-η)-2-butenyl]palladium (29) were prepared by the same route as the triphenylphosphine complex **9**. **27**: mp 150–190 °C dec; ^{13}C NMR δ 133.76 (d, J = 13.1 Hz, Ph-2), 132.46 (d, J = 41.4 Hz, Ph-1), 130.14 (d, J = 2.0 Hz, Ph-4), 128.32 (d, J = 10.3 Hz, Ph-3), 116.95 (d, J = 4.2 Hz, C-2), 99.59 (d, J = 27.0 Hz, C-3), 56.29 (C-1), 17.25 (d, J = 4.1 Hz, CH_3). **29**: mp 114–115 °C; ^{13}C NMR δ 150.69 (d, J = 5.1 Hz, Ph-1), 129.71 (Ph-3), 125.34 (d, J = 1.2 Hz, Ph-4), 121.42 (d, J = 5.5 Hz, Ph-2), 117.25 (d, J = 9.5 Hz, C-2), 101.54 (d, J = 42.7 Hz, C-3), 51.82 (C-1), 17.32 (d, J = 6.5 Hz, CH_3); ^1H NMR δ 4.84 (dt, H_2), 4.17 (m, J_P = 15.8 Hz, H_{3a}), 2.98 (d, H_{1s}), 1.79 (d, H_{1a}), 1.70 (dd, J_P = 16.1 Hz, CH_3).

Chloro(triethyl phosphite)[(1,2,3-η)-2-butenyl]palladium (28) was prepared the same way as the tributylphosphine complex **8**: ^{13}C NMR δ 117.64 (d, J = 9.0 Hz, C-2), 101.15 (d, J = 41.4 Hz, C-3), 61.45 (CH_2O), 50.55 (d, J = 5.5 Hz, C-1), 17.05 (d, J = 7.1 Hz, CH_3), 16.39 (d, J = 6.6 Hz, CH_3CH_2O).

(Pyridine)(triphenylphosphine)[(1,2,3-η)-2-butenyl]palladium tetrafluoroborate (30) (pyridine)(triphenyl phosphite)[(1,2,3-η)-2-butenyl]palladium tetrafluoroborate (31), and (acetonitrile)(triphenylphosphine)[(1,2,3-η)-2-bute-

nyl]palladium tetrafluoroborate (32) were all prepared in about 85% yield by the procedure used for the complex **10**. **30**: ^{13}C NMR δ 151.45 (py-2), 138.20 (py-4), 133.45 (d, J = 13.4 Hz, Ph-2), 130.90 (Ph-4), 130.50 (d, J = 40.2 Hz, Ph-1), 129.02 (d, J = 10.4 Hz, Ph-3), 126.04 (py-3), 120.35 (d, J = 4.5 Hz, C-2), 101.54 (d, J = 25.3 Hz, C-3), 54.20 (C-1), 16.90 (d, J = 3.0 Hz, CH_3); ^1H NMR δ 5.84 (dt, H_2), 4.97 (m, J_P = 8.7 Hz, H_{3a}), 3.47 (d, H_{1s}), 2.94 (d, H_{1a}), 1.42 (dd, J_P = 8.5 Hz, CH_3). In solution the compound disproportionates partly to the corresponding symmetric complexes **15** and **22**. **31**: mp 113–115 °C dec; ^{13}C NMR 151.30 (py-2), 150.03 (d, J = 4.9 Hz, Ph-1), 138.54 (py-4), 130.36 (Ph-3), 126.20 (py-3), 125.97 (d, J = 1.5 Hz, Ph-4), 121.39 (d, J = 8.8 Hz, C-2), 120.85 (d, J = 5.6 Hz, Ph-2), 104.09 (d, J = 37.1 Hz, C-3), 52.44 (d, J = 3.5 Hz, C-1), 16.66 (d, J = 6.4 Hz, CH_3); ^1H NMR δ 5.40 (dt, H_2), 4.72 (m, J_P = 14.7 Hz, H_{3a}), 3.43 (br, H_{1s}), 2.55 (br, H_{1a}), 1.41 (dd, J_P = 15.2 Hz, CH_3). **32**: mp 137–138 °C dec; ^{13}C NMR δ 133.63 (d, J = 13.4 Hz, Ph-2), 131.31 (d, J = 3.0 Hz, Ph-4), 130.67 (d, J = 43.2 Hz, Ph-1), 129.22 (d, J = 10.4 Hz, Ph-3), 124.00 (CN), 119.55 (d, J = 4.5 Hz, C-2), 105.38 (d, J = 24.0 Hz, C-3), 55.02 (C-1), 17.93 (CH_3), 2.49 (CH_3CN); ^1H NMR δ 5.67 (dt, H_2), 5.02 (m, J_P = 8.7 Hz, H_{3a}), 3.37 (dd, H_{1s}), 2.78 (dd, H_{1a}), 1.90 (dd, J_P = 9.2 Hz, CH_3). Anal. Calcd for $C_{24}H_{25}BF_4NPPd$: C, 52.3; H, 4.6; N, 2.5. Found: C, 51.8; H, 4.5; N, 2.4.

Bis(methylamine)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (34) was prepared as a crude oil by the same procedure as used for complex **13**: ^{13}C NMR δ 110.40 (C-2), 87.91 (C-3), 53.22 (C-1), 33.80, 30.88 (CH_3N), 25.72 (CH_{3s}), 20.71 (CH_{3a}).

(Tetramethylethylenediamine)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (35), bis(benzylamino)-[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (36), bis(triphenylphosphine oxide)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (37), and bis(pyridine)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (38) were prepared by the procedure described for the TMEDA complex **1**. **35**: ^{13}C NMR δ 112.14 (C-2), 88.45 (C-3), 61.15, 59.76 (CH_2N), 56.15 (C-1), 52.48, 51.15, 49.94, 48.96 (CH_3N), 25.71 (CH_{3s}), 20.62 (CH_{3a}); ^1H NMR δ 5.28 (dd, H_2), 3.59 (dd, H_{1s}), 3.11 (dd, H_{1a}), 2.95, 2.80, 2.78, 2.62 (s, CH_3N), 1.46 (s, CH_{3s}), 1.21 (s, CH_{3a}). **36**: mp 109–110 °C dec; ^{13}C NMR δ 139.79, 139.12 (Ph-1), 128.92, 128.69, 128.41, 128.10 (10 C, Ph), 109.83 (C-2), 89.07 (C-3), 52.91 (C-1), 50.32, 48.42 ($PhCH_2N$), 25.85 (CH_{3s}), 20.88 (CH_{3a}); ^1H NMR δ 4.89 (dd, H_2), 3.7 (m, CH_2N), 3.29 (dd, H_{1s}), 2.54 (dd, H_{1a}), 1.30 (s, CH_{3s}), 1.02 (s, CH_{3a}). **37**: ^{13}C NMR δ 132.97 (d, J = 2.4 Hz, Ph-4), 131.93 (d, J = 10.3 Hz, Ph-2), 129.58 (d, J = 106.8 Hz, Ph-1), 128.78 (d, J = 12.5 Hz, Ph-3), 104.75 (C-2), 91.72 (C-3), 50.75 (C-1), 26.81 (CH_{3s}), 21.25 (CH_{3a}). **38**: mp 105–106 °C dec; ^{13}C NMR 151.90, 150.77 (br, py-2), 138.79 (py-4), 126.25 (py-3), 112.67 (C-2), 92.18 (C-3), 55.59 (C-1), 26.18 (CH_{3s}), 21.01 (CH_{3a}); ^1H NMR δ 5.54 (dd, H_2), 3.86 (dd, H_{1s}), 3.33 (dd, H_{1a}), 1.37 (s, CH_{3s}), 1.24 (s, CH_{3a}).

Bis(acetone)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (39) was prepared by a similar procedure as the butenyl complex **16**: ^{13}C NMR δ 215.12 (CO), 108.47 (C-2), 94.20 (C-3), 54.22 (C-1), 31.80 (CH_3CO), 26.66 (CH_{3s}), 21.60 (CH_{3a}); ^1H NMR δ 5.37 (dd, H_2), 4.05 (dd, H_{1s}), 3.26 (dd, H_{1a}), 1.34 (s, CH_{3s}), 1.26 (s, CH_{3a}).

Bis(μ-chloro)bis[(1,2,3-η)-3-methyl-2-butenyl]palladium (40) was prepared the same way as the compound **3** by a known procedure:[21] ^{13}C NMR δ 106.35 (C-2), 95.05 (C-3), 55.76 (C-1), 27.12 (CH_{3s}), 21.88 (CH_{3a}).

Bis(acetonitrile)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (41) was prepared by the procedure used for the corresponding propenyl complex **4**: mp 86–88 °C; ^{13}C NMR δ 121.52 (CN), 111.14 (C-2), 98.83 (C-3), 56.77 (C-1), 27.10 (CH_{3s}), 21.63 (CH_{3a}), 2.61 (CH_3CN); ^1H NMR δ 5.26 (dd, H_2), 4.04 (dd, H_{1s}), 3.20 (dd, H_{1a}), 2.39 (CH_3CN), 1.56 (s, CH_{3s}), 1.31 (s, CH_{3a}).

Bis(triphenylphosphine sulfide)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (42), [1,2-bis(phenylthio)ethane][(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (43), [1,2-bis(diphenylphosphino)ethane]-[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (44), bis(triethylphosphine)[(1,2,3-η)-3-methyl-2-butenyl]-palladium tetrafluoroborate (46), bis(tributylphosphine)-[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (47), [(1,2,5,6-η)-1,5-cyclooctadiene][(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (48), bis(trimethyl phosphite)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (49), bis(triphenylarsine)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (50), bis(triphenylphosphine)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (51), bis[tris(4-chlorophenyl)phosphine])-[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (52), and bis(triphenyl phosphite)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (53) were all prepared from the bis(acetonitrile) complex **41** or the cyclooctadiene complex **48** by the addition of 2 equiv of the appropriate ligands as described for the TMEDA complex **1** or, for the bidentate ligand complexes, by the addition of 1 equiv of the ligand. An alternative procedure to prepare the cyclooctadiene complex **48** was also used: To the dimeric chloride complex **40** (4.2 g, 20 mmol), dissolved in 30 mL of dichloromethane, was added cyclooctadiene (2.7 g, 25 mmol). After the mixture was stirred for 20 min, a solution of $AgBF_4$ (3.92 g, 20 mmol) in 20 mL of acetone was added. After the mixture was stirred for 30 min, the precipitated silver chloride was removed by filtration. The solvent and excess of cyclooctadiene were removed under vacuum (oil pump). The crude product was dissolved in 50 mL of dichloromethane, and addition of 150–200 mL of diethyl ether gave **48** (7.2 g, 97%) as yellow crystals. **42**: mp 133–138 °C dec; ^{13}C NMR δ 132.99 (Ph-4), 132.55 (d, J = 10.5 Hz, Ph-2), 128.98 (d, J = 12.8 Hz, Ph-3), 128.91 (d, J = 84.1 Hz, Ph-1), 108.31 (C-2), 105.68 (C-3), 59.19 (C-1), 27.02 (CH_{3s}), 21.69 (CH_{3a}); ^1H NMR δ 4.58 (dd, H_2), 2.94 (dd, H_{1s}), 2.22 (br d, H_{1a}), 1.37 (s, CH_{3s}), 0.98 (s, CH_{3a}). **43**: oil at room temperature; ^{13}C NMR 133.5, 131.0, 130.5 (br, Ph), 114.72 (C-2), 108.27 (C-3), 63.64 (C-1), 40.66 (br, CH_2), 28.09 (CH_{3s}), 22.01 (CH_{3a}); ^1H NMR δ 5.74 (dd, H_2), 4.52 (dd, H_{1s}), 3.72 (dd, H_{1a}), 1.77 (s, CH_{3s}), 1.45 (s, CH_{3a}). **44**: mp 97–98 °C; ^{13}C NMR δ 134.07, 132.65, 132.51, 131.47 (d, J = 11.9–14.1 Hz, Ph-2), 132.61, 132.04, 131.76, 131.49 (d, J = 2.0-2.5 Hz, Ph-4), 130.85 (dd, J = 43.2, 1.7 Hz), 129.65, 129.41, 127.83 (d, J = 38.0 Hz, all Ph-1), 129.98, 129.94, 129.61, 129.58 (d, J = 10.1–11.2 Hz, Ph-3), 115.45 (t, J = 6.7 Hz, C-2), 108.67 (dd, J = 27.5, 6.7 Hz, C-3), 61.00 (dd, J = 29.8, 4.5 Hz, C-1), 28.60 (dd, J = 31.3, 14.1 Hz) and 27.14 (dd, J = 32.0, 13.6 Hz), both CH_2, 27.03 (d, J = 4.5 Hz, CH_{3s}), 20.42 (d, J = 5.2 Hz, CH_{3a}); ^1H NMR δ 5.47 (dd, H_2), 4.27 (tt, J_P = 8.0, 1.0 Hz, H_{1s}), 3.15 (ddd, J_P = 10.0 Hz, H_{1a}), 1.81 (dd, J_P = 9.8, 8.1 Hz, CH_{3s}), 0.96 (app t, J_P = 6.3 Hz, CH_{3a}). **46**: mp 138–142 °C dec; ^{13}C NMR δ 112.80 (t, J = 5.5 Hz, C-2), 112.79 (dd, J = 28.0, 3.7 Hz, C-3), 56.72 (d, J = 29.5 Hz, C-1), 27.29 (d, J = 3.7 Hz, CH_{3s}), 20.86 (d, J = 5.3 Hz, CH_{3a}), 18.25, 15.27 (d, J = ca. 23 Hz, CH_2P), 8.57, 8.18 (CH_3CH_2P); ^1H NMR δ 5.13 (dd, H_2), 3.70 (ddd, J_P = 6.6 Hz, H_{1s}), 2.79 (ddd, J_P = 10.0 Hz, H_{1a}), 2.10 (dd, J_P = 10.5, 5.1 Hz, CH_{3s}), 1.92 (quint, J_P = 7.8 Hz, CH_2P), 1.81 (dq, J_P = 9.5 Hz, CH_2P), 1.34 (dd, J_P = 6.1, 4.9 Hz, CH_{3a}), 1.12 (dt, J_P = 8.5 Hz, CH_3CH_2P), 1.03 (dt, J_P = 7.9 Hz, CH_3CH_2P). **47**: mp 66–67 °C dec; ^{13}C NMR δ 112.84 (dd, J = 26.1, 3.5 Hz, C-3), 112.75 (app t, J = 5.9 Hz, C-2), 57.00 (d, J = 30.5 Hz, C-1), 27.46 (d, J = 4.0 Hz, CH_{3s}), 26.86, 26.39 (s, Bu-2), 25.94, 22.91 (d, J = 23.0 Hz, Bu-1), 24.25, 24.21 (d, J = 13.5 Hz, Bu-3), 20.94 (d, J = 5.4 Hz, CH_{3a}), 13.70 (s, Bu-4); ^1H NMR δ 5.13 (dd, H_2), 3.73 (ddd, J_P = 6.5 Hz, H_{1s}), 2.80 (ddd, J_P = 9.7 Hz, H_{1a}), 2.09 (dd, J_P = 10.3, 5.0 Hz, CH_{3s}) (CH_{3a} is hidden by ligand protons). **48**: decomp 220–225 °C; ^{13}C NMR δ 119.09, 115.78, 114.12, 112.67 (HC=CH), 118.03 (C-2), 114.27 (C-3), 67.27 (C-1), 29.76 (2 C), 29.05, 28.31 (CH_2), 27.48 (CH_{3s}), 21.86 (CH_{3a}); ^1H NMR δ 6.38, 6.29, 5.72, 5.60 (m, br, HC=CH), 5.78 (dd, H_2), 4.61 (dd, H_{1s}), 3.73 (dd, H_{1a}), 1.94 (s, CH_{3s}), 1.56 (s, CH_{3a}). **49**: mp 42–43 °C; ^{13}C NMR δ 115.70 (dd, J = 38.8, 8.9 Hz, C-3), 115.70 (app t, J = 10.3 Hz, C-2), 59.08 (dd, J = 41.9, 5.8 Hz, C-1), 52.59, 52.54 (d, J = 2.5 Hz), 27.00 (d, J = 6.1 Hz, CH_{3s}), 20.66 (d, J = 8.3 Hz, CH_{3a}); ^1H NMR δ 5.45 (dd, H_2), 4.27 (m, J_P = 11.0, 2.7 Hz, H_{1s}), 3.74, 3.73 (d, J_P = 12.3 Hz, CH_3OP), 3.13 (m, J_P = 15.4, 2.0 Hz, H_{1a}), 2.17 (dd, J_P = 16.4, 10.5 Hz, CH_{3s}), 1.44 (t, J_P = 9.8 Hz, CH_{3a}). **50**: *mp 195–210 °C dec*; ^{13}C NMR δ 133.34, 132.92 (Ph-2), 133.14, 131.74 (Ph-1), 130.61 (Ph-4), 129.40 (Ph-3), 117.09 (C-3), 113.05 (C-2), 65.09 (C-1), 26.54 (CH_{3s}), 21.67 (CH_{3a}); ^1H NMR δ 5.76 (dd, H_2), 4.04 (dd, H_{1s}), 3.30 (dd, H_{1a}), 1.36, 1.32 (s, CH_{3s} and CH_{3a}). **51**: mp 178–179 °C dec; ^{13}C NMR δ 133.74, 133.47 (d, J = 13.4 Hz, Ph-2), 131.04 (dd, J = 43.2, 2.0 Hz) and 129.55 (d, J = 40.2 Hz), both Ph-1, 130.98 (d, J = 2.2 Hz, Ph-4), 128.94, 128.90 (d, J = ca. 11 Hz, Ph-3), 119.43 (dd, J = 24.6, 4.5 Hz, C-3), 113.75 (t, J = 6.0 Hz, C-2), 65.65 (dd, J = 28.3, 2.2 Hz, C-1), 25.47 (d, J = 4.5 Hz, CH_{3s}), 21.13 (d, J = 5.2 Hz, CH_{3a}); ^1H

NMR δ 5.68 (dd, H_2), 3.66 (dt, J_P = 7.2 Hz, H_{1s}), 2.89 (ddd, J_P = 9.6 Hz, H_{1a}), 1.17 (dd, J_P = 6.7, 5.1 Hz, CH_{3s}), 1.14 (dd, J_P = 10.8, 6.3 Hz, CH_{3s}). **52**: mp 165–168 °C dec; ^{13}C NMR 136.63 (d, J = 1.8 Hz) and 136.57 (d, J = 2.3 Hz), both Ph-4, 134.07, 133.87 (d, J = 11.2 Hz, Ph-2), 129.66 (d, J = 8.9 Hz, Ph-3), 129.14 (dd, J = 35.1, 1.3 Hz) and 127.96 (dd, J = 32.7, 0.9 Hz), both Ph-1, 121.17 (dd, J = 24.5, 3.9 Hz, C-3), 114.78 (app t, J = 5.2 Hz, C-2), 67.49 (d, J = 25.5 Hz, C-1), 26.03 (d, J = 4.2 Hz, CH_{3s}), 21.50 (d, J = 5.6 Hz, CH_{3a}); ^1H NMR δ 5.89 (dd, H_2), 3.79 (dt, J_P = 8.8 Hz, H_{1s}), 3.05 (ddd, J_P = 9.9 Hz), 1.27 (dd, J_P = 11.0, 6.2 Hz, CH_{3s}), 1.25 (t, J_P = 6.5 Hz, CH_{3a}). **53**: mp 168–170 °C dec; ^{13}C NMR δ 150.18, 149.62 (d, J = 6.2 Hz, Ph-1), 130.53, 130.41 (Ph-3), 126.46 (d, J = 1.2 Hz) and 126.22, both Ph-4, 124.42 (dd, J = 35.2, 8.0 Hz, C-3), 120.63, 120.21 (d, J = ca. 6 Hz, Ph-2), 114.65 (app t, J = 10.9 Hz, C-2), 60.22 (dd, J = 38.5, 4.7 Hz, C-1), 27.48 (dd, J = 6.5, 1.6 Hz, CH_{3s}), 21.26 (d, J = 8.3 Hz, CH_{3a}); ^1H NMR δ 4.99 (ddd, J_P = 1.8 Hz, H_2), 3.14 (tq, J_P = 10.6, 2.3 Hz, H_{1s}), 2.12 (dd, J_P = 17.9, 10.6 Hz, CH_{3s}), 1.86 (t, J_P = 14.0 Hz, H_{1a}), 1.00 (t, J_P = 10.5 Hz, CH_{3a}). Anal. Calcd for $C_{41}H_{39}BF_4O_6P_2Pd$: C, 55.8; H, 4.45; P, 7.0. Found: C, 56.0; H, 4.4; P, 6.9.

Bis(methyl isocyanide)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (45) was prepared by treating the dimeric chloride complex **40** (1 mmol) dissolved in 5 mL of dichloromethane with a solution of $AgBF_4$ (1 mmol) in 2 mL of acetone. After the mixture was stirred for 10 min, the precipitated silver chloride was removed by filtration. The ligand, dissolved in 2 mL of dichloromethane, was added, and after the solution was stirred for 10 minutes, the product was crystallized at 0 °C by adding 20–40 mL of diethyl ether: yield 85%; mp 102–103 °C; ^{13}C NMR δ 136.25, 134.10 (NC), 114.61 (C-2), 108.95 (C-3), 59.35 (C-1), 29.74 (CH_3NC), 28.02 (CH_{3s}), 21.59 (CH_{3a}); ^1H NMR (−45 °C) δ 5.22 (dd, H_2), 4.28 (dd, H_{1s}), 3.60 (s, CH_3N), 3.15 (dd, H_{1a}), 2.09 (CH_{3s}), 1.47 (CH_{3a}); ^1H NMR (room temperature) δ 5.22 (t, H_2), 4.5–3.0 (2 H, H_{1s}, H_{1a}), 3.58 (CH_3N), 2.07 (CH_{3s}), 1.46 (CH_{3a}).

Cyano(triphenylphosphine)[(1,2,3-η)-3-methyl-2-butenyl]palladium (54) was prepared the same way as the corresponding butenyl complex **24**. It darkens without melting at 95–105 °C. **54**: ^{13}C NMR δ 142.89 (CN), 133.65 (d, J = 12.6 Hz, Ph-2), 132.86 (d, J = 41.7 Hz, Ph-1), 130.38 (d, J = 2.0 Hz, Ph-4), 128.52 (d, J = 10.7 Hz, Ph-3), 113.62 (C-2), 107.37 (C-3), 56.94 (C-1), 28.00 (CH_{3s}), 21.32 (CH_{3a}). No phosphorus coupling to the allyl unit is observed, indicating rapid ligand exchange. ^1H NMR: δ 5.14 (dd, H_2), 2.94 (dd, H_{1s}), 2.58 (dd, H_{1a}), 2.26 (d, J_P = 8.9 Hz, CH_{3s}), 1.51 (d, J_P = 5.3 Hz, CH_{3a}).

Chloro(methyl isocyanide)[(1,2,3-η)-3-methyl-2-butenyl]palladium (55) was prepared by the procedure used for the phosphine complex **8** by addition of methyl isocyanide to the bridged chloride complex **40**: mp 89–90 °C; ^{13}C NMR δ 140 (br m, NC), 109.84 (C-2), 108.80 (C-3), 50.37 (C-1), 29.44 (br, CH_3NC), 26.26 (CH_{3s}), 20.77 (CH_{3a}); ^1H NMR δ 5.02 (dd, H_2), 3.83 (dd, H_{1s}), 3.40 (CH_3NC), 2.91 (dd, H_{1a}), 1.78 (CH_{3s}), 1.35 (CH_{3a}).

(*SP*-4-3)-[1-Amino-2-(diphenylphosphino)ethane][(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (56) was prepared by the procedure used for the TMEDA complex **1**, the only difference being that the cyclooctadiene complex **48** was used as starting material instead of the bis(acetonitrile) complex **41**: mp 143–145 °C dec; ^{13}C NMR δ 132.78, 132.66 (d, J = 13.4 Hz, Ph-2), 131.82, 131.11 (d, J = 59.0 Hz, Ph-1), 131.26 (Ph-4), 129.24, 129.14 (d, J = 9.8 Hz, Ph-3), 112.6 (d, J = 25.6 Hz, C-3), 111.6 (d, J = 3.7 Hz, C-2), 46.5 (d, J = 2.4 Hz, C-1), 42.3 (d, J = 6.1 Hz, CH_2N), 32.2 (d, J = 26.9 Hz, CH_2P), 26.7 (d, J = 3.6 Hz, CH_{3s}), 20.9 (d, J = 3.7 Hz, CH_{3a}); ^1H NMR δ 7.65–7.3 (br m, Ph), 5.20 (dd, H_2), 4.25–4.1 (br m, NH), 3.75–3.6 (br m, NH), 3.63 (dd, H_{1s}), 3.3–2.8 (br m, CH_2N), 2.76 (dd, H_{1a}), 2.65–2.45 (br m, CH_2P), 2.06 (d, J_P = 8.5 Hz, CH_{3s}), 1.56 (d, J_P = 5.1 Hz, CH_{3a}). Small amounts of the isomer **75** are detectable by ^{13}C NMR: δ 134.20 (d, J = 14.6 Hz, Ph-2), 129.72 (d, J = 9.8 Hz, Ph-3), 116.5 (d, J = 4.7 Hz, C-2), 88.3 (d, J = 6.1 Hz, C-3), 67.8 (d, J = 28.1 Hz, C-1), 42.0 (d, J = 7.3 Hz, CH_2N), 32.5 (d, J = 25.6 Hz, CH_2P), 28.3 (CH_{3s}), 21.1 (CH_{3a}); ^1H NMR (tentative) δ 5.3 (dd, H_2), 4.6 (t, H_{1s}), 4.0 (m, H_{1a}), 1.52 (d, J_P = ca. 7 Hz, CH_{3a}), 0.98 (d, J_P = 6.0 Hz, CH_{3a}).

Chloro(tributylphosphine)[(1,2,3-η)-3-methyl-2-butenyl]palladium (57) was prepared the same way as the corresponding propenyl complex **8**: ^{13}C NMR δ 114.53 (d, J = 25.9 Hz, C-3), 108.36 (d, J = 4.4 Hz, C-2), 42.32 (d, J = 2.0 Hz, C-1), 26.65 (Bu-2), 26.05 (d, J = 4.6 Hz, CH_{3s}), 25.07 (d, J = 23.1 Hz, Bu-1), 24.25 (d, J = 13.3 Hz, Bu-3), 20.39 (d, J = 4.7 Hz, CH_{3a}), 13.58 (Bu-4).

Iodo(triphenylphosphine)[(1,2,3-η)-3-methyl-2-butenyl]palladium (58) was prepared according to the procedure used for the cyanide complex **24** by shaking a dichloromethane solution of the chloride complex **64** with an aqueous solution of KI: mp 178–180 °C dec; ^{13}C NMR δ 134.23 (d, J = 12.7 Hz, Ph-2), 133.37 (d, J = 41.8 Hz, Ph-1), 130.28 (d, J = 1.8 Hz, Ph-4), 128.38 (d, J = 10.4 Hz, Ph-3), 114.99 (d, J = 26.7 Hz, C-3), 111.38 (d, J = 4.7 Hz, C-2), 57.89 (d, J = 1.6 Hz, C-1), 29.08 (d, J = 4.3 Hz, CH_{3s}), 22.12 (d, J = 5.0 Hz, CH_{3a}); ^1H NMR δ 5.09 (dd, H_2), 3.18 (dd, H_{1s}), 2.89 (dd, H_{1a}), 2.38 (d, J_P = 9.6 Hz, CH_{3s}), 1.42 (d, J_P = 6.5 Hz, CH_{3a}).

(Isothiocyanato)(triphenylphosphine)[(1,2,3-η)-3-methyl-2-butenyl]palladium (59) was prepared by treating the chloride dimeric complex **40** (1 mmol), dissolved in 5 mL of acetone, with a solution of $AgBF_4$ (1 mmol) in 3 mL of acetone. After removal of silver chloride, triphenylphosphine and then KSCN were added. The solution was stirred for 30 min, the solvent was evaporated, and the residue was recrystallized from diethyl ether–petroleum ether: mp 50–55 °C; ^{13}C NMR δ 133.70 (d, J = 13.0 Hz, Ph-2), 131.83 (d, J = 41.7 Hz, Ph-1), 130.68 (Ph-4), 128.72 (d, J = 10.4 Hz, Ph-3), 115.2 (br d, J = ca. 25 Hz, C-3), 110.9 (s, C-2), 56 (br, C-1), 25.8 (s, CH_{3s}), 20.3 (s, CH_{3a}); ^1H NMR δ 7.7–7.3 (br m, Ph), 5.18 (t, H_2), 3.1 (br m, H_{1s}), 2.9 (br m, H_{1a}), 2.06 (d, J_P = 9.6 Hz, CH_{3s}), 1.53 (d, J_P = 6.0 Hz, CH_{3a}).

(*SP*-4-3)-[1-(Dimethylamino)-2-(diphenylphosphino)ethane][(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (60) was prepared from **41** by the procedure used for the diphos complex **5**: mp 128–130 °C; ^{13}C NMR δ 132.63 (d, J = 13.3 Hz, Ph-2), 131.73, 131.69 (d, J = 46.2 Hz, Ph-1), 131.7 (br m, Ph-4), 129.57, 129.49 (d, J = 10.2 Hz, Ph-3), 115.21 (d, J = 26.5 Hz, C-3), 111.19 (d, J = 5.0 Hz, C-2), 61.71 (d, J = 7.4 Hz, CH_2N), 50.00 (CH_3N), 43.64 (d, J = 3.4 Hz, C-1), 28.48 (d, J = 26.9 Hz, CH_2P), 25.98 (d, J = 3.8 Hz, CH_{3s}), 20.42 (d, J = 4.8 Hz, CH_{3a}); ^1H NMR δ 5.35 (dd, H_2), 3.49 (dd, H_{1s}), 2.83, 2.78 (s, CH_3N), 2.72 (H_{1a}), 1.98 (d, J_P = 9.5 Hz, CH_{3s}), 1.51 (d, J_P = 5.4 Hz, CH_{3a}). The H_{1a} signal overlaps with the ligand methylene protons and was only visible after decoupling.

In solution, **60** isomerizes to give a 5:2 ratio of **60** and the isomer **72**: ^{13}C NMR δ 134.07 (d, J = 14.3 Hz, Ph-2), 118.62 (d, J = 5.7 Hz, C-2), 85.58 (d, J = 5.0 Hz, C-3), 73.52 (d, J = 28.3 Hz, C-1), 61.04 (d, J = 7.2 Hz, CH_2N), 53.91, 51.96 (s, CH_3N), 30.66 (d, J = 25.4 Hz, CH_2P), 27.75 (CH_{3s}), 21.08 (CH_{3a}); ^1H NMR δ 5.64 (dd, H_2), 4.47 (dd, J_P = 6.2 Hz, H_{1s}), 3.84 (dd, J_P = 9.2 Hz, H_{1a}), 3.10, 2.92 (s, CH_3N), 1.42 (d, J_P = 8.5 Hz, CH_{3s}), 0.97 (d, J_P = 6.1 Hz, CH_{3a}).

(SP)-4-3)-{2-[(Diphenylphosphino)methyl]pyridine}-[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (61) was prepared as the bis(methyl isocyanide) complex **45**: softens at 90 °C; mp 108–110 °C; ^{13}C NMR δ 159.64 (d, J = 6.1 Hz, Pic-2), 150.28 (Pic-6), 140.45 (Pic-4), 132.56 (d, J = 13.5 Hz, Ph-2), 131.79 (d, J = 1.9 Hz, Ph-4), 129.54 (d, J = 11.0 Hz, Ph-3), 125.87 (d, J = 8.1 Hz, Pic-3), 124.90 (Pic-5), 115.3 (d, J = 28.0 Hz, C-3), 111.67 (d, J = 5.7 Hz, C-2), 45.34 (d, J = 4.0 Hz, C-1), 40.19 (d, J = 28.6 Hz, CH_2), 25.7 (d, J = 4.7 Hz, CH_{3s}), 21.0 (d, J = 5.0 Hz, CH_{3a}); ^1H NMR δ 8.5 (d, J_P = 5 Hz, Pic-6), 8.0–7.3 (br m, Ph, Pic), 5.43 (app t, H_2), 4.4–4.2 (br m, PCH_2), 3.7 (br m, H_{1s}), 3.0 (br m, H_{1a}), 2.08 (d, J_P = 10.2 Hz, CH_{3s}), 1.61 (d, J_P = 6.2 Hz, CH_{3a}) (Pic = picolyl).

In solution, **61** isomerizes to give small amounts of the isomer **73**: ^{13}C NMR δ 158.96 (d, J = 6.0 Hz, Pic-2), 155.97 (Pic-6), 140.18 (Pic-4), 133.42 (d, J = 13.6 Hz, Ph-2), 131.85 (Ph-4), 129.61 (d, J = 11.0 Hz, Ph-3), 125.44 (d, J_P = 8.2 Hz, Pic-3), 124.48 (Pic-5), 118.8 (d, J = 6.0 Hz, C-2), 86.2 (d, J = 4.0 Hz, C-3), 73.3 (d, J = 29.0 Hz, C-1), 41.37 (d, J = 27.4 Hz, CH_2P), 27.8 (d, J = 1.5 Hz, CH_{3s}), 21.6 (CH_{3a}); ^1H NMR δ 8.95 (d, J_P = ca. 5 Hz, Pic-6), 8.0–7.3 (br m, Ph, Pic), 5.72 (dd, H_2), 4.64 (app t, H_{1s}), 4.4–4.0 (br m, CH_2P, H_{1a}), 1.45 (d, J_P = 9.4 Hz, CH_{3s}), 1.21 (d, J_P = 6.5 Hz, CH_{3a}).

Chloro(tricyclohexylphosphine)[(1,2,3-η)-3-methyl-2-butenyl]palladium (62) was generated in situ the same way as the tributylphosphine complex **8**: ^{13}C NMR δ 115.50 (d, J = 23.1 Hz, C-3), 107.68 (d, J = 3.9 Hz, C-2), 41.87 (d, J = 2.5 Hz, C-1), 34.59 (d, J = 18.2 Hz, Cy-1), 30.30 (d, J = 3.0 Hz, Cy-2), 27.55 (d, J

= 10.8 Hz, Cy-3), 26.44 (d, J = 1.0 Hz, Cy-4), 26.13 (d, J = 4.4 Hz, CH_{3s}), 20.51 (d, J = 4.4 Hz, CH_{3a}).

Chloro(triphenylphosphine)[(1,2,3-η)-3-methyl-2-butenyl]palladium (64) and chloro(triphenyl phosphite)[(1,2,3-η)-3-methyl-2-butenyl]palladium (68) were prepared by the same procedure as the triphenylphosphine complex **9**. **64**: mp 174–177 °C dec; ^{13}C NMR δ 133.86 (d, J = 13.0 Hz, Ph-2), 132.80 (d, J = 41.5 Hz, Ph-1), 130.14 (Ph-4), 128.37 (d, J = 10.5 Hz, Ph-3), 116.54 (d, J = 25.5 Hz, C-3), 110.22 (d, J = 4.5 Hz, C-2), 52.23 (C-1), 26.78 (d, J = 4.5 Hz, CH_{3s}), 20.79 (d, J = 5.0 Hz, CH_{3a}); ^1H NMR δ 5.18 (dd, H_2), 2.80 (dd, H_{1s}), 2.71 (dd, H_{1a}), 1.94 (d, J_P = 9.0 Hz, CH_{3s}), 1.48 (d, J_P = 5.6 Hz, CH_{3a}). **68**: ^{13}C NMR δ 150.78 (d, J = 4.6 Hz, Ph-1), 129.68 (Ph-3), 125.29 (d, J = 1.6 Hz, Ph-4), 121.49 (d, J = 5.6 Hz, Ph-2), 120.05 (d, J = 39.5 Hz, C-3), 110.05 (d, J = 9.1 Hz, C-2), 47.52 (d, J = 5.2 Hz, C-1), 26.31 (d, J = 7.7 Hz, CH_{3s}), 20.30 (d, J = 8.3 Hz, CH_{3a}); ^1H NMR δ 4.65 (dd, H_2), 2.77 (dt, J_P = 1 Hz, H_{1s}), 1.94 (dd, H_{1a}), 1.79 (d, J_P = 15.6 Hz, CH_{3s}), 0.98 (d, J_P = 10.0 Hz, CH_{3a}).

(Pyridine)(triphenylphosphine)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (63) and (methyl isocyanide)(triphenylphosphine)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (65) were prepared from the complex **64** by the procedure used for the propenyl complex **10**. **63**: mp 135–150 °C dec; ^{13}C NMR δ 150.74 (py-2), 138.45 (py-4), 133.37 (d, J = 13.4 Hz, Ph-2), 131.02 (d, J = 2.2 Hz, Ph-4), 130.22 (d, J = 43.2 Hz, Ph-1), 129.13 (d, J = 11.2 Hz, Ph-3), 126.44 (py-3), 116.22 (d, J = 23.8 Hz, C-3), 112.60 (d, J = 4.5 Hz, C-2), 50.01 (C-1), 25.79 (d, J = 3.7 Hz, CH_{3s}), 20.71 (d, J = 4.5 Hz, CH_{3a}); ^1H NMR δ 5.65 (dd, H_2), 3.42 (dd, H_{1s}), 2.82 (dd, H_{1a}), 1.51 (d, J_P = 4.5 Hz, CH_{3s}), 1.49 (d, J_P = 8.8 Hz, CH_{3a}). **65**: mp 145–147 °C; ^{13}C NMR δ 138.59 (d, J = 18.3 Hz, NC), 133.32 (d, J = 13.4 Hz, Ph-2), 131.40 (d, J = 1.5 Hz, Ph-4), 130.53 (probably half of Ph-1 doublet), 129.23 (d, J = 10.7 Hz, Ph-3), 117.49 (d, J = 23.2 Hz, C-3), 113.96 (d, J = 4.9 Hz, C-2), 59.08 (d, J = 1.7 Hz, C-1), 29.6 (br, CH_3NC), 27.97 (d, J = 3.5 Hz, CH_{3s}), 21.75 (d, J = 4.9 Hz, CH_{3a}); ^1H NMR δ 7.7–7.3 (m, Ph), 5.39 (dd, H_2), 3.53 (dd, H_{1s}), 3.31 (CH_3NC), 2.85 (dd, H_{1a}), 2.31 (d, J_P = 9.6 Hz, CH_{3s}), 1.63 (d, J_P = 5.7 Hz, CH_{3a}).

Chloro(triethyl phosphite)[(1,2,3-η)-3-methyl-2-butenyl]palladium (66) and chloro(trimethyl phosphite)[(1,2,3-η)-3-methyl-2-butenyl]palladium (67) were prepared the same way as the 2-methylpropenyl complex **8**. **66**: ^{13}C NMR δ 118.10 (d, J = 38.6 Hz, C-3), 110.28 (d, J = 8.7 Hz, C-2), 61.39 (Et-1), 46.32 (d, J = 5.6 Hz, C-1), 25.97 (d, J = 7.5 Hz, CH_{3s}), 20.35 (d, J = 7.5 Hz, CH_{3a}), 16.35 (d, J = 6.6 Hz, Et-2). **67**: ^{13}C NMR δ 119.00 (d, J = 38.4 Hz, C-3), 110.39 (d, J = 8.4 Hz, C-2), 52.18 (CH_3O), 46.30 (d, J = 5.4 Hz, C-1), 26.05 (d, J = 7.4 Hz, CH_{3s}), 20.41 (d, J = 7.4 Hz, CH_{3a}).

(Pyridine)(triphenyl phosphite)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (69) and (acetonitrile)(triphenylphosphine)[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (70) were prepared in the same way as the mixed complex **10**. **69**: ^{13}C NMR δ 150.73 (py-2), 150.16 (d, J = 4.6 Hz, Ph-1), 138.77 (py-4), 130.42 (Ph-3), 126.51 (py-3), 126.08 (d, J = 1.5 Hz, Ph-4), 120.90 (d, J = 5.7 Hz, Ph-2), 120.35 (d, J = 33.6 Hz, C-3), 113.00 (dd, J = 8.3 Hz, C-2), 47.55 (d, J = 3.3 Hz, C-1), 25.44 (d, J = 6.8 Hz, CH_{3s}), 20.09 (d, J = 7.4 Hz, CH_{3a}); ^1H NMR δ 5.27 (dd, H_2), 3.20 (dd, H_{1s}), 2.36 (dd, H_{1a}), 1.27 (d, J_P = 19.3 Hz, CH_{3s}), 1.06 (d, J_P = 8.8 Hz, CH_{3a}). In solution, **69** disproportionates partially to give an equilibrium mixture containing also small amounts of the symmetric complexes **38** and **53**. **70**: mp 139–147 °C dec; ^{13}C NMR δ 133.51 (d, J = 13.4 Hz, Ph-2), 131.29 (d, J = 2.2 Hz, Ph-4), 130.59 (d, J = 43.2 Hz, Ph-1), 129.19 (d, J = 11.2 Hz, Ph-3), 123.19 (CN), 122.72 (d, J = 22.3 Hz, C-3), 111.23 (d, J = 3.7 Hz, C-2), 50.76 (C-1), 26.84 (d, J = 3.7 Hz, CH_{3s}), 21.27 (d, J = 4.5 Hz, CH_{3a}), 2.46 (CH_3CN); ^1H NMR δ 5.40 (dd, H_2), 3.26 (dd, H_{1s}), 2.81 (dd, H_{1a}), 2.14 (s, CH_3CN), 2.01 (d, J_P = 8.9 Hz, CH_{3s}), 1.60 (d, J_P = 5.2 Hz, CH_{3a}).

(*SP*-4-3)-{[2-(*N*,*N*-Dimethylhydrazonomethyl)phenyl]diphenylphosphine}[(1,2,3-η)-3-methyl-2-butenyl]palladium tetrafluoroborate (71) was prepared the same way as the diphos complex **5**. **71**: mp 134–136 °C; ^{13}C NMR δ 144.05 (d, J = 3.9 Hz, –CH=N), 136.62 (d, J = 15.0 Hz, Bah-1), 135.61 (d, J = 9.4 Hz, Bah-3) 134.5–132.5 (br m), 132.64, 132.60 (d, J = 16.4 Hz, Ph-2), 131.71 (br), 130.51 (d, J = 7.2 Hz, Bah-4), 129.29 (d, J = 11.1 Hz, Ph-3), 124.36 (d, J = 37.7 Hz, Bah-2), 122.96 (d, J = 23.9 Hz, C-3), 111.61 (d, J = 5.5 Hz, C-2), 44.85 (2 C, NCH_3), 44.70 (d, J = 5.0 Hz, C-1), 26.90 (d, J = 4.4 Hz, CH_{3s}), 21.21 (d, J = 5.0 Hz, CH_{3a}); ^1H NMR δ 5.44 (dd, H_2), 3.28 (dd, H_{1s}), 2.85 (s, CH_3N), 2.76 (dd, H_{1a}), 2.00 (d, J_P = 10.0 Hz, CH_{3s}), 1.50 (d, J_P = 5.4 Hz, CH_{3a}) (Bah = benzaldehyde hydrazone). Anal. Calcd for $C_{26}H_{30}BF_4N_2PPd$: C, 52.5; H, 5.1; N, 4.7. Found: C, 50.1; H, 5.0; N, 4.4. Small amounts of the isomer **74** are detectable by ^{13}C NMR: δ 118.6 (C-2), 86.5 (C-3), 78.2 (C-1), 27.6 (CH_{3s}), 21.5 (CH_{3a}).

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