this hydrogenation is a remarkably mild, stereospecific, selective, and potentially valuable phase-transfer reaction.

The following general procedure was used. To 28 mg (0.063 mmol) of $[1,5\text{-HDRhCl}]_2$ in hexane or benzene (15 mL) was added in sequence: the organic reactant (100/1 ratio of substrate/Rh catalyst), the phase-transfer catalyst (0.3–0.5 mmol), and 5 mL of the buffer solution. Hydrogen gas was bubbled through the stirred solution at room temperature and atmospheric pressure (reaction was followed by NMR spectroscopy). The layers were separated, and the organic phase was dried and distilled.

Acknowledgment. We are grateful to British Petroleum for support of this research.

Registry No. 1, 98-86-2; $[1,5\text{-HDRhCl}]_2$, 32965-49-4; $PhCH_2COCH_3$, 103-79-7; $PhCH_2CH_2COCH_3$, 2550-26-7; PhC_4H_9, 104-51-8; $PhCOOCH_3$, 93-58-3; $PhCONH_2$, 55-21-0; CH_3COOPh, 122-79-2; C_6H_6, 71-43-2; CTAB, 57-09-0; THS, 16873-13-5; *p*-methylanisole, 104-93-8; naphthalene, 91-20-3; 2-methylpyridine, 109-06-8; quinoline, 91-22-5; isoquinoline, 119-65-3; 2-ethylfuran, 3208-16-0; phenol, 108-95-2.

Unexpected Ortho-metalated Products Resulting from Dibenzoyldiazomethane Activation in the Presence of Iridium Phosphine Complexes

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Summary: The reaction of *trans*-$[IrCl(N_2)(PPh_3)_2]$ with $N_2C(C(O)Ph)_2$ in refluxing toluene yields $[IrCl(HC(C(O)Ph)_2)(P(C_6H_4)Ph_2)(PPh_3)]$ in which one phosphine ligand has undergone ortho-metalation and the hydrogen atom has been transferred to the dibenzoylmethylene moiety yielding a β-diketonate group. In refluxing THF $[IrCl(PPh_3)_3]$ and $N_2C(C(O)Ph)_2$ yield $[IrCl(C_6H_4C(O)CC(Ph)OPPh_2)(PPh_3)_2]$ in which an unusual tridentate ligand has been formed by loss of a phenyl group from PPh_3 and condensation of the dibenzoylmethylene moiety with the PPh_2 fragment. In addition, one phenyl group of this ligand has ortho-metalated.

The chemistry of dibenzoyldiazomethane ($N_2C(C(O)Ph)_2$) with metal complexes offers an added dimension over that usually observed for diazoalkane molecules. In addition to the diverse chemistry that might be expected of the diazo moiety,[1] the carbonyl functional groups may also become involved in the coordination and chemical transformations of this molecule. We have recently observed this phenomenon both in chemistry that involves the intact dibenzoyldiazomethane molecule[2] and in chemistry in which N_2 loss has occurred from this group. It is some novel findings in this latter area that we now wish to communicate.

Dibenzoyldiazomethane reacts with both *trans*-$[IrCl(N_2)(PPh_3)_2]$ and $[IrCl(PPh_3)_3]$. In the reaction of 215 mg (0.28 mmol) of *trans*-$[IrCl(N_2)(PPh_3)_2]$ with 75 mg (0.30 mmol) of $N_2C(C(O)Ph)_2$ in refluxing toluene for 35 min an orange-yellow solution was obtained from which a yellow crystalline material (**1**) could be isolated in 90% yield. The elemental analysis was consistent with the formulation $[IrCl(C(C(O)Ph)_2)(PPh_3)_2]\cdot{}^1/_2C_6H_5CH_3$, and the infrared spectrum showed bands at 1521, 1541, and 1592 cm^{-1} but showed no bands between 1600 and 2800 cm^{-1}; in particular no band was observed that could be clearly attributed to the diazo or carbonyl moieties or to an Ir–H stretch. The $^{31}P\{^1H\}$ NMR spectrum (at 36.4 MHz) showed two doublets at δ −2.9 and −82.5 (J_{PP} = 21 Hz); the latter chemical shift is characteristic of an ortho-metalated triphenylphosphine group[3] and the coupling suggested that the phosphines were mutually cis. In the ^1H NMR spectrum (at 400 MHz), a single peak (1 H) was observed at δ 6.80 in addition to the phenyl and toluene resonances, but no resonance was observed upfield in the region expected for a metal hydride.

When the above reaction was carried out in refluxing THF, an additional product, **2**, was observed as a minor component. This species could be obtained as the major product (ca. 80% yield) in the reaction of 97 mg (0.39 mmol) of $N_2C(C(O)Ph)_2$ with 392 mg (0.39 mmol) of $[IrCl(PPh_3)_3]$ in refluxing THF for 40 min. The infrared and ^1H NMR spectra for **2** closely resembled those for **1**, but the $^{31}P\{^1H\}$ NMR spectrum was significantly different, displaying two doublets at δ −11.0 and −69.2 (J_{PP} = 17 Hz), which again suggested that the phosphines were mutually cis with one being ortho-metalated. Complex **2** could be quantitatively converted to **1** by refluxing in toluene for 18 h. Both **1** and **2** are air stable and showed no reactivity toward CO or PPh_3.

Also observed in the preparation of **2** from $[IrCl(PPh_3)_3]$ was a minor product, **3**, in about 10% yield (based on $^{31}P\{^1H\}$ NMR). Its $^{31}P\{^1H\}$ NMR spectrum appeared as a doublet (2 P) at δ −15.7 and a triplet (1 P) at δ 83.7 (J_{PP} = 21 Hz). The infrared spectrum showed medium bands at 1636, 1577, and 1546 cm^{-1}, but no absorptions apart from C–H stretches were observed at higher frequency. The ^1H NMR spectrum of **3** showed only phenyl and toluene resonances. Unambiguous characterization of **1** and **3** was achieved by an X-ray crystal structure determination of each.

Both compounds crystallize with one toluene molecule per unit cell; complex **1** crystallizes in the space group $P\bar{1}$ with $Z = 2$, a = 12.396 (2) Å, b = 19.272 (3) Å, c = 10.742 (1) Å, α = 97.84 (6)°, β = 115.59 (4)°, γ = 78.77 (1)°, and V = 2268.9 $Å^3$; compound **3** crystallizes in the space group $P1$ with $Z = 1$, a = 12.1972 (8) Å, b = 10.163 (1) Å, c = 11.761 (1) Å, α = 103.609 (8)°, β = 95.059 (7)°, γ = 96.619 (7)°, and V = 1397.4 $Å^3$. Data were collected to 2θ = 120° for both structures on an automated Picker FACS-1 diffractometer using Ni-filtered Cu Kα radiation. The structure of compound **1** was solved by standard Patterson and Fourier techniques, whereas that for **3** was solved by difference Fourier techniques after arbitrarily fixing the iridium atom at the origin of the cell.[4] Both data sets were corrected for absorption and the structures refined by

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(1) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800.

(2) Cowie, M.; Loeb, S. J.; McKeer, I. R., manuscript in preparation.

(3) (a) Garrou, P. E. *Inorg. Chem.* **1975**, *14*, 1435. (b) Pregosin, P. S.; Kunz, R. H. "The ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes"; Springer-Verlag, New York, 1979. (c) In the $^{31}P\{^1H\}$ NMR spectrum of $[IrCl(H)(C_6H_4PPh_2)(PPh_3)_2]$ for example, we observe the following parameters: δ 4.2 (dd), −6.0 (dd), −92.2 (dd), J_{PP}(cis) = 10, 18 Hz, J_{PP}(trans) = 370 Hz (dd = doublet of doublets).

(4) $P1$ is a polar space group. The correct enantiomer was established by changing all coordinates (x, y, z) to $(\bar{x}, \bar{y}, \bar{z})$ and comparing subsequent refinements. The wrong enantiomer converged at R = 0.039 and R_w = 0.058. In addition, the polar dispersion error gave rise to a significantly larger spread in chemically equivalent bond distances for the wrong enantiomer. A complete description of the structure will appear.

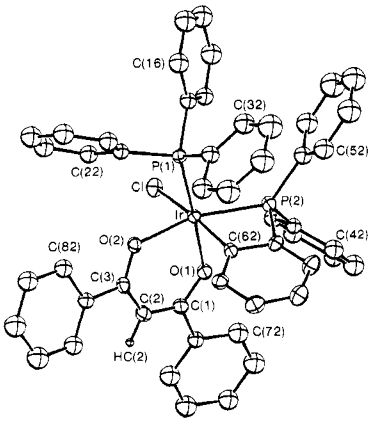

Figure 1. Perspective drawing of compound 1, [$IrCl(HC(C(O)Ph)_2)(P(C_6H_4)Ph_2)(PPh_3)$]. Thermal ellipsoids in both figures are drawn at the 20% level except for HC(2) in compound 1, which is shown artificially small. Some relevant parameters are Ir–P(1) = 2.264 (2) Å, Ir–P (2) = 2.277 (2) Å, Ir–C(62)–C(61) = 107.4 (6)°, and P(2)–Ir–C(62)° = 68.4 (2)°. Other parameters are given in the text.

full-matrix, least-squares techniques; for **1** R = 0.050 and R_w = 0.068[5] for 232 parameters varied and 5140 unique observations; for **3** R = 0.028 and R_w = 0.037 for 266 variables and 4387 unique observations. Refinement was carried out in essentially the same way for both structures; all phenyl groups except the ortho-metalated ones (which were treated as independent atoms) were refined as rigid groups;[6] all independent, non-hydrogen atoms were refined anisotropically and all hydrogens on the complex molecules, although located, were input in idealized positions by using C–H bond distances of 0.95 Å and were not refined. The toluene of crystallization was well behaved in structure **3** but disordered in **1**.

Complex **1** was shown to be a six-coordinate, Ir(III) species as diagrammed in Figure 1. As suggested by the $^{31}P\{^1H\}$ NMR spectrum, the complex contains mutually cis phosphine groups, one of which is ortho-metalated. The structure also confirms that N_2 loss has occurred from the dibenzoyldiazomethane molecule. However, instead of binding to the metal through the carbene carbon, as might be expected, a hydrogen atom transfer to this carbon, C(2), has occurred and the group now binds to the iridium center through both oxygens as a β-diketonate ligand. A somewhat analogous hydrogen transfer to the carbene carbon in the alkylidene fragment, $:C(CH_3)C(O)CH_3$, has been observed to give the coordinated olefin in (η^5-$C_5H_4CH_3$)-$Mo(CO)_2(H_2C{=}CHC(O)CH_3)$,[7] although in this case hydrogen transfer occurred from within the alkylidene unit. In compound **1**, it seems that the hydrogen atom bound to C(2) originates from the ortho-metalated phenyl group. This explains both our failure to detect a metal hydride by spectroscopic techniques and the singlet at δ 6.80 in the ^1H NMR—a region characteristic for a β-diketonate hydrogen.[8]

Although formation of a β-diketonate complex from a diazo diketone was unexpected, the resulting parameters within this complex are as one might expect for such a species. Both Ir–O distances (Ir–O(1) = 2.078 (5) Å and Ir–O(2) = 2.086 (5) Å) are in good agreement with each other and with other determinations involving iridium

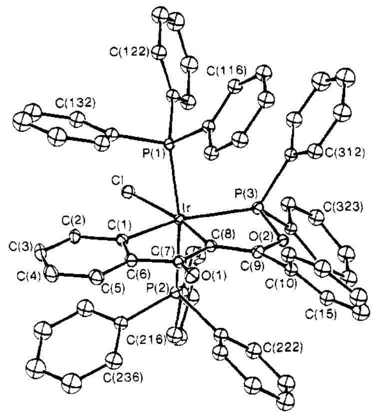

Figure 2. Perspective drawing of compound 3, [$IrCl(C_6H_4C(O)CC(Ph)OPPh_2)(PPh_3)_2$]. Some relevant parameters are (Ir–P(1) = 2.384 (3) Å, Ir–P(2) = 2.380 (3) Å, Ir–P(3) = 2.355 (2) Å, and C(9)–O(2)–P(3) = 118.7 (5)°. Other parameters are given in the text.

diketonates.[8] Within the metal chelate ring the parameters suggest considerable delocalization; the C(1)–O(1) and C(3)–O(2) distances (1.258 (9) and 1.267 (9) Å) and the C(1)–C(2) and C(2)–C(3) distances (1.39 (1) and 1.38 (1) Å) are intermediate between the extremes expected for single and double bonds.[9] The Ir–C(62) distance of 2.027 (8) Å is typical for an ortho-metalated triphenylphosphine group,[10] and the Ir–Cl bond trans to this group shows the expected lengthening (2.474 (2) Å) due to the high trans influence of the metalated carbon.[11] The Ir–P(2)–C(61) and C(62)–C(61)–P(2) angles of 85.6 (3)° and 98.4 (6)° are much smaller than are observed in normal PPh_3 groups and reflect the ring strain imposed by the ortho-metalation.

The structure of **3** (see Figure 2) is also one of a distorted octahedral Ir(III) species in which ortho-metalation has occurred. However, in this case the dibenzoylmethylene moiety, generated by N_2 loss from the diazo diketone, has remained coordinated to the metal at the original methylene carbon position (C(8)) and other very unusual transformations have occurred. At one end of the dibenzoylmethylene fragment, one of the phenyl groups has ortho-metalated while at the other end, it has condensed with a PPh_2 fragment through a carbonyl oxygen atom forming a P–O bond. This P–O linkage has replaced a P–Ph one, presumably via reductive elimination of this phenyl group together with the hydrogen atom from the ortho-metalated group. The result is a highly unusual tridentate ligand which is bonded to Ir through the ortho-metalated carbon C(1), the methylene carbon C(8), and P(3), creating two fused five-membered metallocycles. The structural parameters within these metallocycles are most consistent with the central part of this group binding as a vinyl moiety; therefore, C(8)–C(9) (1.38 (1) Å) is much shorter than the other C–C bonds (C(6)–C(7) = 1.46 (1) Å, C(7)–C(8) = 1.49 (1) Å) and approaches a C–C double bond, although some delocalization throughout the rings is indicated. The exocyclic C(7)–O(1) bond (1.23 (1) Å)

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(5) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(6) Idealized D_{6h} geometry for the carbon atoms was assumed with C–C distances of 1.392 Å.

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(8) Bezman, S. A.; Bird, P. H.; Fraser, A. R.; Osborne, J. A. *Inorg. Chem.* **1980**, *19*, 3755.

(9) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. III, Tables 4.2.2 and 4.2.5.

(10) (a) Perego, G.; del Piero, G.; Cesari, M.; Clerici, M. G.; Perrotti, E. *J. Organomet. Chem.* **1973**, *54*, C51. (b) von Deuten, K.; Dahlenburg, L. *Cryst. Struct. Commun.* **1980**, *9*, 421. (c) del Piero, G.; Perego, G.; Cesari, M.; Clerici, M.; Perrotti, E. *Ibid.* **1974**, *3*, 725.

(11) A "normal" Ir–Cl bond distance falls in the range 2.36–2.39 Å (see: Clark, G. R.; Clark, P. W.; Marsden, K. *J. Organomet. Chem.* **1979**, *173*, 231), whereas Ir–Cl bonds opposite ligands of high trans influence are expected near 2.45–2.48 Å (see: Nolte, M. J.; Singleton, E.; van der Stok, E. *J. Chem. Soc., Chem. Commun.* **1978**, 973, and Schultz, A. J.; McArdle, J. V.; Khare, G. P.; Eisenberg, R. *J. Organomet. Chem.* **1974**, *72*, 45.)

corresponds to a normal C–O double bond whereas the endocyclic C(9)–O(2) distance (1.407 (9) Å) is close to that of a single bond. The P(3)–O(2) distance (1.632 (5) Å) is comparable to analogous distances in phosphite ligands.[12] Both Ir–C bonds are normal (Ir–C(1) = 2.093 (7) Å, Ir–C(8) = 2.046 (9) Å) and the Ir–Cl bond (2.475 (2) Å), which is almost identical with that in compound **1**, reflects the high trans influence of C(8). The geometry about P(3) shows the strain imposed by the metallocycle. Thus, the Ir–P(3)–O(2) angle (100.6 (2) Å) is small, and the two Ir–P(3)–Ph angles (124.6 (2)° and 129.7 (2)°) are significantly larger than those involving the normal PPh_3 groups (average 116.0°). All other angles within the metallocycles are close to their expected values of 120°.

Both compounds **1** and **3** display the well-known tendency of Ir(I) compounds to undergo intramolecular C–H bond activation in the form of ortho-metalation reactions. In neither case, however, is the initial iridium hydride species observed; instead hydrogen transfer in **1** occurs, yielding the β-diketonate group, and in **3** metal activation of a P–Ph bond has resulted in reductive elimination of benzene and the formation of the P–O bond to give a diphenyl phosphinite group.

On the basis of similarities in spectral parameters between **1** and **2** and on the conversion of **1** to **2**, it is assumed at this stage that **2** is a geometrical isomer of **1**. Further studies are underway on these systems in attempts to obtain further information about these unusual dibenzoyldiazomethane activations.

Acknowledgment. We thank the University of Alberta and the National Sciences and Engineering Research Council of Canada for financial support.

Registry No. **1**, 86272-05-1; **2**, 86288-19-9; **3**, 86272-06-2; $IrCl(PPh_3)_3$, 16070-58-9; $N_2C(C(O)Ph)_2$, 2085-31-6; *trans*-$[IrCl(N_2)(PPh_3)_2]$, 21414-18-6.

Supplementary Material Available: Tables summarizing the crystal data and intensity collection details, positional and thermal parameters and a listing of observed and calculated structure amplitudes (37 pages). Ordering information is given on any current masthead page.

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Oligomerization and Isomerization of Olefins by η^3-Allyl Complexes of Palladium. The Role of the Allyl Group

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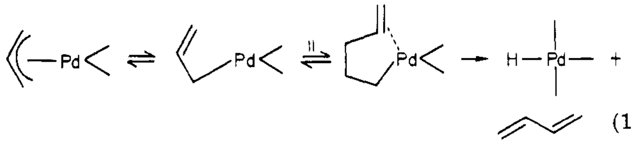
Summary: $[(\eta^3\text{-}C_3H_5)Pd(CD_3NO_2)_2](BF_4)$ is a catalyst for the dimerization and the isomerization of olefins. The allyl group is retained in the course of these catalytic reactions. A carbonium ion mechanism which does not involve the participation of the allyl group is proposed.

We report a series of dimerization and isomerization of olefins catalyzed by $[(\eta^3\text{-}C_3H_5)Pd(CD_3NO_2)_2](BF_4)$, **1a**, *where the allyl group is retained in the course of the reaction.* Cationic, η^3-allyl complexes of Pd(II) prepared either in situ,[1,2] or separately,[3] have been reported to catalyze the oligomerization and cooligomerization of monoolefins,[1] the cooligomerization of monoolefins with dienes,[2] and the telomerization of dienes with alcohols.[3] While the mechanism of these reactions is not well understood, it has been postulated[2d] that the active catalyst is a palladium(II) hydride formed initially by the insertion of an olefin into a σ-allyl–palladium followed by a β-hydrogen abstraction step, eq 1. However, to our knowledge, such a mechanism involving an initial loss of the allyl ligand has never been verified experimentally. On the other hand, our observations clearly indicate that this mechanism is inoperative, at least for the systems that we have studied.



(1)

The cationic η^3-allyl complexes $[(\eta^3\text{-}C_3H_5)Pd(solvent)_2](BF_4)$ (solvents CD_3NO_2, **1a**,[4] and CH_3CN, **1b**[5]) were generated by the addition of 2 equiv of $AgBF_4$ to $[(\eta^3\text{-}C_3H_5)PdCl]_2$,[6] **2**, in an appropriate solvent system. The catalytic properties of **1a** are summarized in Table I. In every case, following the completion of the catalytic reaction, **1a** was recovered in near-quantitative yields,[9] thus ruling out eq 1, at least as the major mechanistic pathway. In order to further confirm this observation, the dimerization of $PhCH{=}CH_2$ was followed by ^1H NMR using a $PhCH{=}CH_2/\mathbf{1a}$ ratio of 1. Again, no species other than 1,3-diphenyl-1-butene[7] and **1a** was observed at the end of the reaction. It may be pointed out that our observations are fully consistent with that of Kurosowa and Asada,[10] who have observed the complete retention of the allyl fragment in the catalytic isomerization of olefins by $[(\eta^3\text{-}CH_2CMeCH_2)Pt(PPh_3)(CH_2{=}CHR)]ClO_4$(R = alkyl).

It is interesting to note that the corresponding neutral μ-chloro dimer **2** was ineffective for the dimerization of $PhCH{=}CH_2$ and $Ph_2C{=}CH_2$ under conditions identical with those employed in case of **1a**. The poor catalytic activity of **2** for the dimerization of C_2H_4 has also been demonstrated.[1a] We have also shown that a higher temperature (80 vs. 25 °C for **1a**) was required for the di-

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[1] (a) Barlow, M. G.; Bryant, M. J.; Haszeldine, R. N.; Mackie, A. G. *J. Organomet. Chem.* **1970**, *21*, 215. (b) Wilke, G. Ger. Offen. 1 520 964, 1974. (c) Hattori, S.; Munakata, H.; Tatsuoka, K.; Shimizu, T. Ger. Offen. 2 234 922, 1974; U.S. Patent 3 803 254, 1974.

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[3] Grenouillet, P.; Neibecker, D.; Poirier, J.; Tkatchenko, I. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 767.

[4] ^1H NMR ($CDCl_3$–CD_3NO_2, ppm): 5.94 (1 H, m), 4.54 (2 H, d, J = 7 Hz), 3.44 (2 H, d, J = 12 Hz).

[5] ^1H NMR ($CDCl_3$–CD_3NO_2, ppm): 5.80 (1 H, m), 4.45 (2 H, d, J = 7 Hz), 3.30 (2 H, d, J = 12 Hz), 2.23 (6 H, s).

[6] Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220.

[7] ^1H NMR ($CDCl_3$, ppm): 7.4–7.2 (10 H, m), 6.38 (2 H, d, J = 5 Hz), 3.63 (1 H, m, J = 5 Hz, 6.9 Hz), 1.45 (3 H, d, J = 6.9 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 145.5, 137.5, 135.1, 128.6–126.1, 42.5, 21.2. Mol wt ($CHCl_3$): found 212; calcd, 208. Hydrogenation product: 1,3-diphenylbutane. ^1H NMR ($CDCl_3$, ppm): 7.3–7.1 (10 H, m); 2.65 (1 H, m, J = 7 Hz, 7 Hz); 2.50 (2 H, t, J = 7.6 Hz); 1.90 (2 H, m, J = 7 Hz, 7.6 Hz); 1.24 (3 H, d, J = 7 Hz).

[8] ^1H NMR ($CDCl_3$, ppm): 7.4–7.0 (19 H, m), 3.45, 3.10 (2 H, ABq, J = 12 Hz), 1.6 (3 H, s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 150.5–147.5, 128.8–125.0, 61.4, 60.9, 51.2, 28.9. Mass spectrum: m/e 360 (M^+).

[9] In the experiment where 1 equiv of PPh_3 was added to **1a** prior to the addition of $PhCH{=}CH_2$ (Table I), an $(\eta^3\text{-}C_3H_5)Pd^{II}$ compound with ^1H NMR shifts slightly different from those of **1a** was observed, presumably due to the coordination of PPh_3. This species was recovered following the catalytic dimerization of $PhCH{=}CH_2$ (Table I).

[10] Kurosowa, H.; Asada, N. *Organometallics* **1983**, *2*, 251.

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