phenylacetylene has been found to possess an activation enthalpy of 26.9 kcal/mol,[4d] qualitatively consistent with our results. Alternatively, the measured activation energy could be associated with a rate-limiting conversion of the metallacycle to the π complex, which would only be valid if the barrier for the reverse reaction (π complex to metallacycle) is similar in magnitude to the olefin binding energy (~10 kcal/mol). This interpretation is inconsistent with our calculated barrier (~0 kcal/mol) but leads to relative thermodynamic placements of the metallacycle and π complex similar to those presented here (eq 2). Finally, an associative mechanism (where both olefins are bound to the alkylidene complex) is possible for our coordinatively unsaturated dichloro complex (the bis(olefin) complex would be a 12-electron system) and in fact has a barrier lower than the dissociative mechanism described above (~10 kcal/mol lower). This associative mechanism is not likely for the experimental dicyclopentadienyl system as the bis(olefin) complex would be a 20-electron system (barring cyclopentadienyl ring slippage) but is possible for other highly coordinately unsaturated systems.

Hoffmann and co-workers[5] have studied the olefin metathesis reaction pathway using the extended Hückel method. The set of complexes they examined included $Cp_2Ti(CH_2)(C_2H_4)$, for which they obtained results diametrically opposed to other theoretical work,[3] experiment,[4] and the work reported here. Specifically, they find the metallacyclobutane substantially less stable than the olefin methylidene complex (by approximately 20 kcal/mol). Further, they find the global potential energy surface minimum to be associated with a geometry close to that found here for the saddle point. This minimum was found to be approximately 6 kcal/mol below the olefin methylidene complex. A point of agreement common to our work, experiment, and Hoffmann and co-workers is that the observed barrier should be small.

The extention of the above results to olefin metathesis (eq 3) in general is straightforward. As discussed above

$$R'_2C{=}CR'_2 + R_2C{=}CR_2 \rightarrow 2R'_2C{=}CR_2 \qquad (3)$$

we find this process to have a very low kinetic barrier. As noted previously[3a,4] the difficulty for titanium systems is the thermodynamic instability of titanium methylidene complexes. For Cr, Mo, and W oxo dichloride methylidene systems, with appropriate cocatalysts, the thermodynamics are balanced.[7] The activation energetics presented here suggests that these Cr, Mo, and W oxo systems will be quite active catalysts with small kinetic and thermodynamic barriers. Thus, our theoretical results are in agreement with the experimental evidence from the Schrock group.[8]

Registry No. $Cl_2TiCH_2(C_2H_4)$, 91158-49-5; dichlorotitanacyclobutane, 79953-32-5; dicyclopentadienyltitanacyclobutane, 80122-08-3.

Supplementary Material Available: Details of computational procedures employed to obtain complex geometries and thermodynamic data (2 pages). Ordering information is given on any current masthead page.

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(7) Rappé, A. K.; Goddard III, W. A. *J. Am. Chem. Soc.*, **1982**, *104*, 448–456.

(8) Schrock, R. R.; Rocklage, S.; Wengrovious, J.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73–83. Wengrovious, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.*, **1980**, *102*, 4515–4516.

"Open Cobaltocene" Chemistry. The Dimerization of Bis(2,4-dimethylpentadienyl)cobalt

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Received October 3, 1983

Summary: The reaction of cobaltous chloride with 2 equiv of the 2,4-dimethylpentadienyl anion (2,4-$C_7H_{11}^-$) leads to a dimeric product in which each cobalt atom is coordinated by an η^5-2,4-C_7H_{11} ligand and by an η^4-butadiene portion of half a bridging 2,4,7,9-tetramethyl-2,4,6,8-decatetraene ligand, which was formed by the intermolecular coupling of two 2,4-C_7H_{11} ligands. The coupled ligand is unusual in that an isomerization from a 1,3,7,9-decatetraene ligand seems to have taken place.

We have recently shown that the pentadienyl ligand forms a wide range of stable compounds with transition metals.[2] Of initial interest have been the bis(pentadienyl)metal complexes, wherein the metal may be titanium, vanadium, chromium, iron, or ruthenium, and a wide range of structural, spectroscopic, chemical, and theoretical studies have now been reported for these "open metallocenes".[2,3] As all of the above compounds possess electron configurations in the range of 14–18 (less than or equal to the noble-gas configuration), it was clearly of interest to investigate the nature of "open metallocenes" formally having even greater electron counts.[4]

The reaction of cobaltous chloride with 2 equiv of the 2,4-dimethylpentadienyl anion in THF at −78 °C leads to the formation of a deep red-brown solution, which seems to initially contain monomeric bis(2,4-dimethylpentadienyl)cobalt.[5] On standing at low temperature, however, slow deposition of a less soluble material takes place, occasionally yielding a homogeneous crop of small crystalline material in yields of up to 80%. Initial analytical and mass spectral data suggested a dimeric formulation,[7] $[Co(C_7H_{11})_2]_2$, which was ultimately confirmed

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(1) NSF Predoctoral Fellow, 1980–1983.

(2) (a) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1983**, *2*, 1220. (b) Stahl, L.; Ernst, R. D. *Ibid.* **1983**, *2*, 1229. (c) Wilson, D. R.; Liu, J.-Z.; Ernst, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 1120. (d) Liu, J.-Z.; Ernst, R. D. *Ibid.* **1982**, *104*, 3737. (e) Ernst, R. D.; Liu, J.-Z.; Wilson, D. R. *J. Organomet. Chem.* **1983**, *250*, 257.

(3) (a) Böhm, M. C.; Eckert-Maksić, M.; Ernst, R. D.; Wilson, D. R.; Gleiter, R. *J. Am. Chem. Soc.* **1982**, *104*, 2699. (b) Böhm, M. C.; Ernst, R. D.; Gleiter, R.; Wilson, D. R. *Inorg. Chem.* **1983**, *22*, 3815. (c) Ernst, R. D.; Wilson, D. R.; Herber, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 1646.

(4) This, of course, assumes that both ligands are η^5 bound, which may not be the case.

(5) (a) The monomeric species may well contain one η^5 and one η^3-pentadienyl ligand.[6] (b) Treatment of the initial solution with ferricinium tetrafluoroborate led to a yellow-orange product, insoluble in pentane but soluble in THF and methylene chloride. A mass spectrum indicated the expected $Co(C_7H_{11})_2BF_4$ composition. A single-crystal X-ray diffraction study was undertaken[5c] and the cobalt atom and BF_4^- unit were readily located. It appeared that two 2,4-dimethylpentadienyl ligands were present, but these were badly disordered. Attempts are being made to prepare this cation as a salt with other anions. (c) Hutchinson, J. P.; Wilson, D. R.; Ernst, R. D., unpublished results.

(6) (a) It can be noted that $(C_5H_5)Cr(C_8H_8)$ has been formulated as a 17-electron complex with an η^6-C_8H_8 ligand,[6b] while $(C_5H_5)Ti(C_8H_8)$ is a 17-electron complex with an η^8-C_8H_8 ligand.[6c] (b) Müller, J.; Menig, H. *J. Organomet. Chem.* **1975**, *96*, 83. (c) Van Oven, H. O.; de Liefde Meijer, H. J. *Ibid.* **1969**, *19*, 373.

(7) (a) Anal. Calcd for $C_{14}H_{22}Co$: C, 67.46; H, 8.90. Found: C, 66.71; H, 9.11. (b) In addition to the expected parent ion (*m/e* 498, relative abundance = 3%), other expected fragments were observed, e.g., Co (59, 12%), C_7H_{11} (95, 29%), and $(C_7H_{11})_2$ (190, 20%). A monomeric fragment (*m/e* 249) was not observed. (c) The crude dimer solutions react cleanly with potential ligands such as phosphites to yield good yields of the appropriate ligand adducts of mono(2,4-dimethylpentadienyl)cobalt.

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Table II. Selected Bond Distances (Å) and Angles (deg) for Bis(2,4-dimethylpentadienyl)cobalt Dimer

Bond Distances

Co–C(1)	2.137 (10)	Co–C(9)	2.134 (7)	C(1)–C(2)	1.463 (12)	C(8)–C(9)	1.513 (11)
Co–C(2)	2.080 (10)	Co–C(10)	2.017 (8)	C(2)–C(3)	1.436 (13)	C(9)–C(10)	1.401 (14)
Co–C(3)	2.086 (9)	Co–C(11)	2.014 (8)	C(3)–C(4)	1.397 (14)	C(10)–C(11)	1.424 (11)
Co–C(4)	2.066 (8)	Co–C(12)	2.087 (8)	C(4)–C(5)	1.402 (14)	C(11)–C(12)	1.434 (11)
Co–C(5)	2.123 (7)	C(12)–C(12′)	1.463 (18)	C(2)–C(6)	1.512 (14)	C(9)–C(13)	1.535 (11)
				C(4)–C(7)	1.531 (13)	C(11)–C(14)	1.512 (12)

Bond Angles

C(1)–C(2)–C(3)	123.8 (9)	C(3)–C(4)–C(7)	118.3 (8)	C(10)–C(9)–C(13)	114.2 (7)
C(1)–C(2)–C(6)	119.1 (8)	C(5)–C(4)–C(7)	119.0 (9)	C(10)–C(11)–C(12)	118.6 (8)
C(2)–C(3)–C(4)	126.0 (8)	C(8)–C(9)–C(10)	123.9 (8)	C(10)–C(11)–C(14)	119.3 (7)
C(3)–C(2)–C(6)	117.0 (8)	C(8)–C(9)–C(13)	111.7 (7)	C(12)–C(11)–C(14)	122.0 (7)
C(3)–C(4)–C(5)	122.5 (8)	C(9)–C(10)–C(11)	123.5 (7)	C(11)–C(12)–C(12′)	123.8 (11)

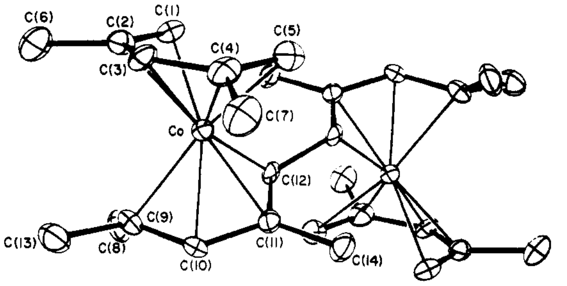
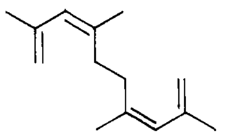


Figure 1. Perspective view of the bis(2,4-dimethylpentadienyl)cobalt dimer. The 20% probability ellipsoids are shown, and a center of inversion is crystallographically imposed.

by a single-crystal X-ray study.[8]

The solid-state structural result shown in Figure 1 clearly confirms the dimeric nature of the product molecule. The dimer itself lies on a crystallographic center of inversion. Each cobalt atom is coordinated by an η^5-2,4-dimethylpentadienyl ligand and to a butadiene portion of half of the 2,4-dimethylpentadienyl dimer in η^4 fashion. Each cobalt atom thereby achieves an 18-electron configuration. The bond distances between a given cobalt atom and its η^5-2,4-C_7H_{11} ligand are slightly longer than the corresponding distances observed for the 18-electron Fe(2,4-$C_7H_{11})_2$ compound—the Co–C(1,5), –C(2,4), and –C(3) distances are 2.130 (6), 2.073 (7), and 2.086 (9) Å, respectively, with the overall average value being 2.098 (4) Å, compared to 2.089 (1) Å for the iron compound. The butadiene ligand appears to be functioning as a normal bis(olefin) donor,[9] as the Co–C(internal) bond distances average 2.016 (6) Å, compared to the longer Co–C(external) bonds (2.111 (6) Å). In Mg(THF)$_3$(*s-cis*-1,4-diphenylbutadiene) the opposite ordering is observed,[10] 2.54 vs. 2.29 Å. The carbon–carbon bond distances are normal.[11]

While the bonding parameters described above are not unusual, the actual form of the dimerized ligand was entirely unexpected. In other reported examples of dimerized pentadienyl ligands, the form of the resulting ligand has to our knowledge always been the expected I[12] (neglecting possible cis/trans isomerization) rather than the isomerized form II that is observed here. The origin of the difference in behavior might, therefore, involve the remaining η^5-2,4-dimethylpentadienyl ligand, since the other examples (e.g., [(C_5H_7)Fe(CO)$_3$]$_2$[12a]) often contained carbonyl ligands. An η^5-pentadienyl ligand is capable of undergoing transformation to an η^3-bound form, thereby leaving the cobalt atom coordinatively unsaturated and capable of bringing about the observed isomerization via a bis(pentadienyl)cobalt hydride.[13] However, even though the above arguments support an η^5–η^3 pentadienyl transformation, they do not completely exclude other mechanisms.[14] Studies designed to better define the actual pathway are in progress.



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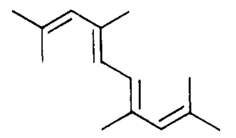

II

Acknowledgment. R.D.E. expresses his gratitude for partial support of this research through grants from the National Science Foundation (#CHE-8120683), from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and from the University of Utah Research Committee. We would also like to acknowledge the National Science Foundation (Grant #CHE-8100424) and the University of Utah Institutional Funds Committee for providing funds for the departmental

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(8) The unit cell was monoclinic of space group $P2_1/c$ with a = 8.468 (6) Å, b = 21.712 (17) Å, c = 7.433 (3) Å, β = 111.73 (4)°, and Z = 2 dimeric units. The structure was solved by standard heavy-atom techniques and refined to final anisotropic agreement indices of R = 0.060 and R_w = 0.048 for the 1154 independent reflections for which $0° < 2\theta < 50°$ and $I > 2.5\sigma(I)$. Hydrogen atoms were included in idealized positions with isotropic thermal parameters, while non-hydrogen atoms were treated anistropically. A final difference fourier map revealed no peaks greater than 0.43 e/Å^3.

(9) Mingos, D. M. P. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 19.

(10) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Yasuda, H.; Nakamura, A. *Chem. Lett.* **1982**, 1277.

(11) For the pentadienyl ligand, the average delocalized C–C bond distance was 1.425 (7) Å (C(1)–C(5)), whereas for the coordinated butadiene portion the average was 1.420 (7) Å (C(9)–C(12)). In neither case could a distinction be made between the "internal" and "external" C–C bonds. The C–C bond distance between coordinated butadiene portions (C(12)–C(12′)) is 1.463 (18) Å.

(12) (a) Jotham, R. W.; Kettle, S. F. A.; Moll, D. B.; Stamper, P. J. *J. Organomet. Chem.* **1976**, *118*, 59. (b) Sapienza, R. S.; Riley, P. E.; Davis, R. E.; Pettit, R. *Ibid.* **1976**, *121*, C35. (c) Connelly, N. G.; Kelly, R. L.; Kitchen, M. C.; Mills, R. M.; Stansfield, R. F. D.; Shiteley, M. W.; Whiting, S. M.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 1317. (d) Bleeke, J. R.; Kotyk, J. J. *Organometallics* **1983**, *2*, 1263.

(13) (a) The hydride intermediate would presumably possess an η^3-pentadienyl ligand together with an η^5-pentadienyl ligand formed from the dimeric fragment. Related (cyclohexadienyl)metal hydride compounds have been reported.[12b–d] (b) Fischer, M. B.; James, E. J.; McNeese, T. J.; Nyburg, S. C.; Posin, B.; Wong-Ng, W.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4941. (c) Blackborow, J. R.; Eady, C. R.; Grevels, F.-W.; Koerner von Gustorf, E. A.; Scrivanti, A.; Wolfbeis, O. S.; Benn, R.; Brauer, D. J.; Krüger, C.; Roberts, P. J.; Tsay, Y.-H. *J. Chem. Soc., Dalton Trans.* **1981**, 661. (d) Baudrey, D.; Ephritikhine, M.; Felkin, H.; Jeanin, Y.; Robert, F. *J. Organomet. Chem.* **1981**, *220*, C7.

(14) One alternative recognized by us, but also emphasized by a reviewer, involves initial η^4–η^2 transformation of the coupled butadiene ligands, rather than the η^5–η^3 pentadienyl transformation, to produce the active cobalt intermediate. However, it is again noted that in cases in which the dimer did not have a remaining pentadienyl ligand, such isomerizations did not occur, even though η^4–η^2 butadiene transformations could still take place. There are, in addition, other electronic[15] and overlap[2,3] reasons to expect the η^5–η^3 transformation to be facile.

(15) Mingos, D. M. P.; Nurse, C. R. *J. Organomet. Chem.* **1980**, *184*, 281.

purchase of the mass spectrometer system.

Registry No. $Co(C_7H_{11})_2BF_4$, 91228-14-7; $[Co(C_7H_{11})_2]_2$, 91208-79-6; cobaltous chloride, 7646-79-9.

Supplementary Material Available: A listing of atomic parameters (Table I) and the structure amplitude table (6 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of a Mononuclear Copper(I) Complex Containing the Copper(I) σ-Phenyl Functionality

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Summary: Reaction of [(triphos)CuCl] [triphos = 1,1,1-tris[(diphenylphosphino)methyl]ethane, $MeC(CH_2PPh_2)_3$] with lithium phenyl in tetrahydrofuran afforded the mononuclear complex [(triphos)CuPh], containing a phenyl group σ bonded to copper(I) with a Cu-C bond distance of 2.020 (4) Å. Copper(I) is in a pseudotetrahedral geometry provided by the triphos ligand and the phenyl group.

Copper(I) alkyl or copper(I) aryl is one of the most interesting organometallic functionalities.[1,2] Its chemistry, however, has to be related to either the bonding mode of the carbon donor ligand or the nature of the ancillary ligands around the metal.[1] This relationship, however, has not been established because of the lack of structural information available.[1,2] Carbon donor ligands are normally engaged in multinuclear structures, where they display a two-electron, three-center bonding mode.[2,3] In such compounds the carbon donor ligand has never been structurally found to display a terminal bonding mode, like that expected in the model L_nCu-Ar (L_n = ancillary ligands) compound, except for a recent reported dimesitylcuprate(I) derivative.[4] The bonding mode of an anionic ligand is, however, always changing from a neutral to a cuprate(I)-type complex[5] and its reactivity, too.[1]

The tridentate tripod-like ligand 1,1,1-tris[(diphenylphosphino)methyl]ethane, $[MeC(CH_2PPh_2)_3]$, triphos, provides the appropriate coordination sphere around copper(I) in order to force the fourth ligand to display a terminal bonding mode.[6] Using triphos as the ancillary ligand, we achieved the stabilization of the first monomeric phenylcopper complex.

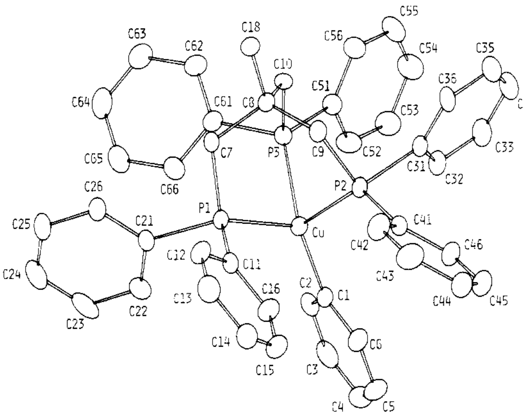
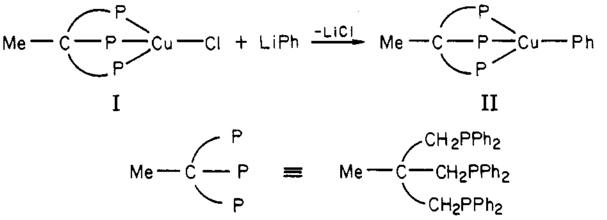


Figure 1. ORTEP drawing of complex II [(triphos)CuPh] (30% probability ellipsoids). Bond distances (Å): Cu-P1 = 2.342 (2), Cu-P2 = 2.276 (2), Cu-P3 = 2.295 (2), and Cu-C1 = 2.020 (4). Bond angles (deg): P3-Cu-C1 = 124.8 (1), P2-Cu-C1 = 126.9 (1), P1-Cu-C1 = 119.4 (1), P2-Cu-P3 = 93.3 (1), P1-Cu-P3 = 91.9 (1), and P1-Cu-P2 = 90.9 (1).

Copper(I) chloride (1 mol) was dissolved in a THF solution of *N,N,N',N'*-tetramethylethylenediamine (1 mol) and then the mixture reacted with triphos. The solution on standing gave white crystals of [(triphos)CuCl][7,8] (I). This procedure must be used in order to obtain I as a crystalline solid suitable for an X-ray analysis.[8] The structure of I is suggested on the basis of preliminary results from an X-ray study.

A THF suspension of I was reacted with an equimolar amount of LiPh in THF. The bright yellow solution was concentrated, followed by addition of Et_2O. The final solution gave on standing for 24 h crystals of II (ca. 60%).[9]



(1)

It is difficult to define the influence that the phosphorous donor ligands can have on the stability of copper-carbon bond, very significant differences being observed with bidentate[10] or monodentate[11] phosphines. An important distinction must be made, however, on whether the synthesis of (phosphine)alkyl- or (phosphine)arylcopper(I) complexes is carried out by the reaction of phosphine ligands with the preformed copper(I) organometallic species or by the alkylation of the corresponding phosphine halo complexes. Crystallographic details for complexes II are as follows: $C_{47}H_{44}CuP_3$, orthorhombic, space group $Pna2_1$ (from systematic absences and structural analysis),

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[‡] Università di Parma.

(1) Jukes, A. E. *Adv. Organomet. Chem.* **1974**, *12*, 215. Posner, G. H. "An Introduction to Synthesis Using Organocopper Reagents"; Wiley: New York, 1980. Normant, J. F. *Pure Appl. Chem.* **1978**, *50*, 709.

(2) Van Koten, G.; Noltes, J. G. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W. Eds.; Pergamon Press, Oxford, 1981; Vol. II, Chapter 14, pp 709-763. Camus, A.; Marsich, N.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta* **1977**, *23*, 131.

(3) Edwards, P. G.; Gellert, R. W.; Marks, M. W.; Bau, R. *J. Am. Chem. Soc.* **1982**, *104*, 2072 and references therein. Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1156.

(4) Leoni, P.; Pasquali, M.; Ghilardi, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 240.

(5) Jardine, F. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 115.

(6) Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4096.

(7) Sacconi, L.; Midollini, S. *J. Chem. Soc., Dalton Trans.* **1972**, 1213.

(8) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C., unpublished results.

(9) Anal. Calcd for $C_{47}H_{44}P_3Cu$: C, 73.77; H, 5.75; P, 12.16. Found: C, 72.96; H, 5.83; P, 12.11.

(10) Camus, A.; Marsich, N.; Nardin, G.; Randaccio, L. *J. Organomet. Chem.* **1973**, *60*, C39. Van Koten, G.; Noltes, J. G.; Spek, A. L. *Ibid.* **1978**, *159*, 441.

(11) Miyashita, A.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1102, 1109.

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