Synthesis of Platinum Bis(phosphonium ylide) Complexes from α-Halomethyl Precursors

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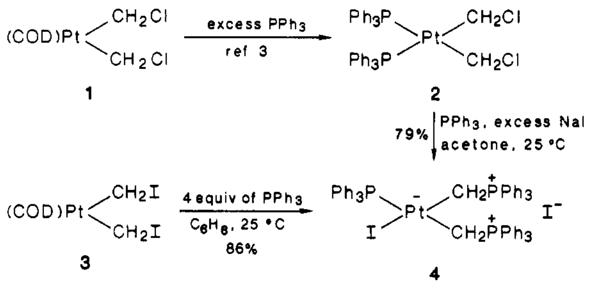
Summary: In contrast to the reported reaction of triphenylphosphine with (COD)Pt($CH_2Cl)_2$, excess triphenylphosphine reacts with (COD)Pt($CH_2I)_2$ to give the interesting zwitterionic bis(phosphonium ylide) complex [(Ph_3P)(I)Pt($CH_2PPh_3)_2$]I, which has been characterized spectroscopically and by crystallography [space group $P2_1/c$; cell dimensions (at −155 °C) a = 14.308 (4), b = 17.354 (5), c = 19.082 (5) Å, β = 90.39 (1)°; Z = 4; V = 4738.15 Å^3, d(calcd) = 1.771 g cm^{-3}; $R_w(F)$ = 0.064 for 4199 independent reflections]. Complete substitution by four phosphines is observed by using trimethylphosphine, affording [($Me_3P)_2$Pt($CH_2PMe_3)_2$]I_2.

The synthesis and chemistry of transition-metal phosphonium ylide complexes have been extensively investigated.[1,2] Interest in this class of organometallic complexes arises principally because these complexes may be important intermediates in catalytic reactions and are considered potential catalysts for new processes. Additionally, however, ylide complexes are beginning to be exploited in stoichiometric organometallic chemistry as versatile substrates for further synthetic manipulation:[2a-e] essentially the same reason phosphonium ylides are used so extensively in organic synthesis.

The majority of transition-metal phosphonium ylide complexes have been prepared by halide metathesis using preformed phosphorus ylides (Wittig reagents).[1,2c,f-i] These complexes have also, but less frequently, been synthesized from haloalkyl precursors by displacement using trialkyl- or triarylphosphine nucleophiles.[1,2a,j] In this paper, we report the synthesis of several platinum bis(phosphonium ylide) complexes by the displacement strategy and demonstrate that the course of such displacement reactions can be controlled by changes in the substrate and entering nucleophile.

Scheme I



For a project designed to synthesize oxygen- and nitrogen-substituted platinacyclobutane complexes, we required as starting materials platinum bis(halomethyl) complexes containing several types of ancillary ligands. We anticipated entering the series of required complexes based on the recent report by McCrindle et al.,[3] describing the straightforward exchange of the 1,5-cyclooctadiene ligand in (COD)Pt($CH_2Cl)_2$ (1) for triphenylphosphine (Scheme I). Because in our hands the corresponding bis(iodomethyl) complex 3, also reported by McCrindle, could be prepared more reproducibly in higher yield, this material was selected for subsequent exchange reactions.

Unexpectedly, treatment of (COD)Pt($CH_2I)_2$ (3) with 2 equiv of triphenylphosphine in benzene or tetrahydrofuran at room temperature or below led to a complex mixture of products. The major product from this reaction became the only product when 3 or more equiv of triphenylphosphine was used, and in benzene this material precipitated from the reaction mixture. The pale yellow, air-stable product was isolated in >85% yield and identified on the basis of spectroscopic analysis[4] to be the novel zwitterionic bis(phosphonium ylide) complex 4 (Scheme I). Identical material was also obtained in high yield from ($Ph_3P)_2$Pt($CH_2Cl)_2$ (2) by treatment with 1 equiv of triphenylphosphine and an excess of NaI in acetone at room temperature. The ^{1}H NMR and ^{13}C NMR spectra[4] were fully consistent with the proposed structure and with previous correlations of structure with ^{195}Pt–^{1}H coupling constants.[5] The ^{31}P NMR spectrum confirmed the presence of three inequivalent phosphines, but only one bonded directly to the metal (J_{Pt-P} = 2650 Hz).

Single crystals of bis(ylide) 4 were obtained from methanol/ether solution, and the structure was confirmed by X-ray crystallography.[6] The molecular geometry and atom-labeling scheme are given in Figure 1, along with selected bond distances and angles. The structure is unremarkable except for the degree of steric crowding in the coordination sphere of the metal, which results in some distortion from idealized square-planar geometry. No unusually short distance between the anionic platinum and either positively charged ylide phosphorus is observed in the solid state. A compositionally analogous complex of

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(1) Reviews: Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907. Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1. Weber, L. In *The Chemistry of the Metal*-Carbon Bond; Hartley, H. R., Patai, S., Eds.; New York: Wiley, 1982; Vol. 1, Chapter 3.

(2) (a) Zolk, R.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 233. (b) Usón, R.; Laguna, A.; Laguna, M.; Usón, A.; Gimeno, M. C. *Organometallics* **1987**, *6*, 682. (c) Facchin, G.; Bertani, R.; Calligaris, M.; Nardin, G.; Mari, M. *J. Chem. Soc., Dalton Trans.* **1987**, 1381. (d) Alt, H. G.; Hayen, H. I. *J. Organomet. Chem.* **1986**, *316*, 301. Huy, N. H. T.; Fischer, E. O.; Alt, H. G.; Dötz, K. H. *J. Organomet. Chem.* **1985**, *284*, C9. (e) Crocco, G. L.; Gladyz, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1154. Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141. (f) Lai, R.; Le Bot, S.; Baldy, A.; Pierrot, M.; Arzoumanian, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1208. (g) Schumann, H.; Albrecht, I.; Reier, F.-W.; Hahn, E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 522. (h) Schmidbaur, H.; Pichl, R.; Müller, G. *Chem. Ber.* **1987**, *120*, 39 and references therein. (i) Erker, G.; Czisch, P.; Krüger, C.; Wallis, J. M. *Organometallics* **1985**, *4*, 2059. (j) Weber, L.; Wewers, D.; Boese, R. *Chem. Ber.* **1985**, *118*, 3570. Weber, L.; Wewers, D. *Organometallics* **1985**, *4*, 841. (k) Murray, H.; Fackler, J. P., Jr.; Porter, L. C.; Briggs, D. A.; Guerra, M. A.; Lagow, R. J. *Inorg. Chem.* **1987**, *26*, 357 and references therein. (l) Schmidbaur, H.; Hartmann, C.; Riede, J.; Huber, B.; Müller, G. *Organometallics* **1986**, *5*, 1652 and references therein. (m) Vincente, J.; Chicote, M. T.; Cayuelas, J. A.; Fernandez-Baeza, J.; Jones, P. G.; Sheldrick, G. M.; Espinet, P. *J. Chem. Soc., Dalton Trans.* **1985**, 1163. (n) Azam, K. A.; Frew, A. A.; Lloyd, B. R.; Manajlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 1400. (o) Lin, I. J. B.; Kao, L. T. C.; Wu, F. J.; Lee, G. H.; Wang, Y. *J. Organomet. Chem.* **1986**, *309*, 225. (p) Facchin, G.; Campostrini, R.; Michelin, R. A. *J. Organomet. Chem.* **1985**, *294*, C21.

(3) McCrindle, R.; Arsenault, G. J.; Farwaha, R. *J. Organomet. Chem.* **1985**, *296*, C51.

(4) Spectroscopic data for complex 4: mp >200 °C (open tube, no dec); IR (KBr) 3025, 2900, 1580, 1480, 1435, 1100, 740, 690 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80–7.04 (m, 45 H), 2.52 (dd, J_{P-H} = 15.2, 9.0 Hz, J_{Pt-H} = 73.3 Hz, 2 H), 1.75 (dd, J_{P-H} = 12.3, 7.8 Hz, J_{Pt-H} = 98.2 Hz, 2 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 135.5 (d, J_{P-C} = 8.7 Hz), 134–133 (complex), 131.9 (d, J_{P-C} = 53.2 Hz), 130.9 (s), 130.5 (d, J_{P-C} = 10.6 Hz), 129.7 (d, J_{P-C} = 83.2 Hz), 122.9 (d, J_{P-C} = 82.2 Hz); $^{31}P\{^1H\}$ NMR (146 MHz, $CDCl_3$) δ 28.28 (d, J_{P-P} = 8.9 Hz, J_{Pt-P} = 44.6 Hz), 25.01 (s, J_{Pt-P} = 60.3 Hz), 17.97 (d, J_{P-P} = 8.9 Hz, J_{Pt-P} = 2650 Hz). Anal. Calcd for $C_{56}H_{49}I_2P_3Pt$: C, 53.22; H, 3.91. Found: C, 53.42; H, 4.06.

(5) Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247. Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1972**, *11*, 2749, and references therein.

0276-7333/88/2307-2082$01.50/0

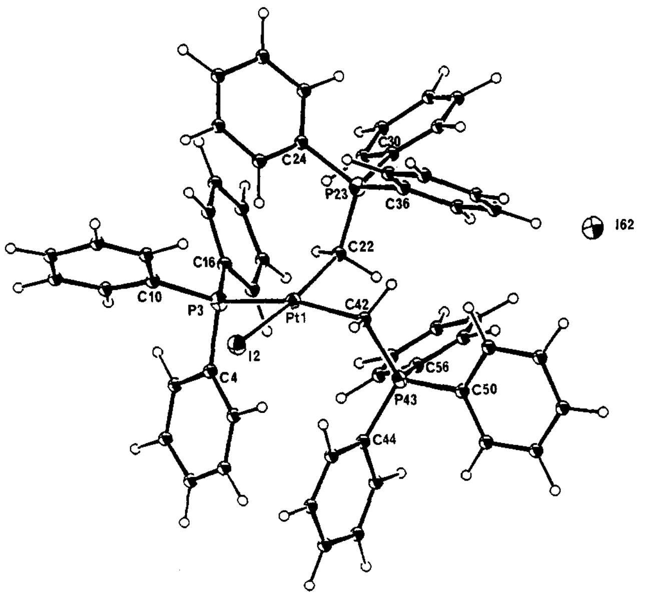
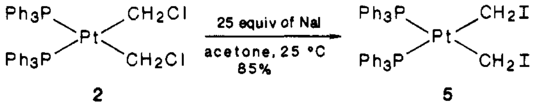


Figure 1. ORTEP drawing of complex **4a**. Selected bond distances (Å): Pt(1)-I(2), 2.679 (2); Pt(1)-P(3), 2.296 (6); Pt(1)-C(22), 2.095 (21); Pt(1)-C(42), 2.084 (22); P(23)-C(22), 1.788 (22); P(43)-C(42), 1.833 (22). Selected nonbonding distances (Å): Pt(1)-P(23), 3.349 (8); Pt(1)-P(43), 3.272 (9). Selected bond angles (deg): I(2)-Pt(1)-P(3), 91.45 (14); I(2)-Pt(1)-C(22), 169.5 (6); I(2)-Pt(1)-C(42), 88.8 (6); P(3)-Pt(1)-C(22), 93.3 (6); P(3)-Pt(1)-C(42), 165.4 (6); C(22)-Pt(1)-C(42), 89.0 (8); Pt(1)-C(22)-P(23), 119.0 (11); Pt(1)-C(42)-P(43), 113.1 (11).

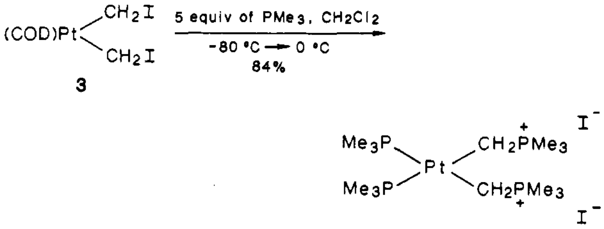
nickel has been reported from the reaction of trimethylphosphonium methylide with $(Me_3P)_2NiCl_2$ in pentane.[7,8]

The failure to isolate the expected $(Ph_3P)_2Pt(CH_2I)_2$ (**5**) from the ligand replacement reaction can be rationalized by assuming that nucleophilic displacement of iodide becomes competitive with cyclooctadiene replacement in the bis(iodomethyl) complex, consistent with the well-established rate acceleration for S_N2-type nucleophilic displacements involving iodide rather than chloride as the leaving group.[9] At this point, it is difficult to determine whether this competition occurs upon initial interaction with triphenylphosphine or after 1 equiv has reacted at the metal center. The thermodynamic stability of $(Ph_3P)_2Pt(CH_2I)_2$ (**5**) is not in question: this material can be synthesized in good yield from $(Ph_3P)_2Pt(CH_2Cl)_2$ by treatment with a large excess of NaI in acetone (eq 1)[10] and is relatively stable in solution in the absence of additional triphenylphosphine.[11]



2 **5** (1)

In an attempt to drive the ylide-forming reaction to the fully substituted bis(phosphine) bis(phosphonium ylide) complex, the use of the less sterically demanding and more electron-rich trimethylphosphine was investigated. Treatment of complex **3** with an excess of trimethylphosphine below room temperature in dichloromethane resulted in the immediate precipitation of a white solid. Analytically pure material was obtained in 84% yield after recrystallization from methanol/ether and was identified by elemental and spectroscopic analysis to be the fully substituted bis(ylide) complex **6** (eq 2).[12] A high degree of molecular symmetry was strongly suggested by the simplicity of the NMR data. The ^1H NMR spectrum revealed a single resonance for the two methylene groups. This signal appeared as a doublet of doublets: no coupling between the methylenes and the cis phosphine ligand was observed.[13] The $^{13}C\{^1H\}$ NMR spectrum similarly revealed a single resonance for the methylene groups, coupled inequivalently to three phosphorus nuclei, as expected for the cis geometry in the proposed structure. At J_{Pt-C} = 530 Hz, the ^{195}Pt satellites for this resonance are consistent with carbon trans to strongly electron-donating trimethylphosphine.[5] Again most definitive was the ^{31}P NMR spectrum, which showed only two multiplets more than 50 ppm apart in chemical shift. The coupling in this spectrum was determined to be second order, AA′XX′, neglecting platinum satellites, and the signal multiplicites were duplicated and coupling constants extracted by NMR simulation techniques.[14]



3 **6** (2)

In summary, depending on the nature of the phosphine and the identity of the halide substituent on the alkyl moiety, the balance between ligand replacement at the metal and nucleophilic substitution at the halide can be influenced. By judicious choice of substrate and ligand, simple replacement of cyclooctadiene by two phosphine ligands, bis(ylide) formation to zwitterionic products, or

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(6) X-ray crystallography was carried out by Dr. John C. Huffman at the Indiana University Department of Chemistry Molecular Structure Center. Crystal data for compound 4, $PtC_{56}H_{49}I^+I^-$: space group $P2_1/c$; cell dimensions (at −155 °C) a = 14.308 (4), b = 17.354 (5), c = 19.082 (5) Å, β = 90.39(1)°; Z (molecules/cell) = 4; V = 4738.15 Å^3 d(calcd) = 1.771 g cm^{-3}; wavelength = 0.71069 Å, linear absorption coefficient = 44.183 cm^{-1}, max absorption = 0.6690, min absorption = 0.7510. The structure was solved by using a combination of direct methods and Fourier techniques and was refined to final residuals $R(F) = 0.077$ and $R_w(F) = 0.064$ for 4199 independent reflections ($F > 2.33\sigma(F)$) of 6226 unique intensities collected in the range $6.0 \leq 2\theta \leq 45.0°$. Details of the data collection and structure solution, atomic positional and thermal parameters, complete bond distance and angle data, and a listing of F_o vs F_c are included as supplementary material.

(7) Karsch, H. H.; Schmidbaur, H. *Chem. Ber.* **1974**, *107*, 3684.

(8) A variety of less closely related Ni, Pd, and Pt phosphonium ylide complexes have been reported. See ref 1.

(9) See: Streitwieser, A., Jr. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962; p 30 and references therein.

(10) Spectroscopic data for complex **5**: mp >200 °C (open tube, slight dec); IR (KBr) 3060, 1960, 1480, 1435, 1095, 1070, 740, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 (t, J = 8.6 Hz, 12 H), 7.28 (t, J = 6.8 Hz, 6 H), 7.17 (t, J = 7.2 Hz, 12 H), 2.93 (d, J_{P-H} = 10.2 Hz, J_{Pt-H} = 32.0 Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.8 (m), 131.3 (d, J_{P-C} = 48.4 Hz), 129.9 (s), 127.8 (m), 12.1 (dd, J_{P-C} = 118.1, 7.5 Hz, J_{Pt-C} not resolved); ^{31}P NMR (146 MHz, $CDCl_3$) δ 22.98 (s, J_{Pt-P} = 2047 Hz). Anal. Calcd for $C_{38}H_{34}I_2P_2Pt$: C, 45.57; H, 3.42. Found: C, 44.81; H, 3.37.

(11) While no tendency for rearrangement to ylide-containing complexes is observed, not unexpectedly, $(Ph_3P)_2Pt(CH_2I)_2$ decomposes slowly in solution, giving $(Ph_3P)_2PtI_2$ and ethylene via a solvolytic pathway. See: McCrindle, R.; Arsenault, G. J.; Farwaha, R.; Hampden-Smith, M. J.; McAlees, A. J. *J. Chem. Soc., Chem. Commun.* **1986**, 943.

(12) Spectroscopic data for compound **6**: mp 174–175 °C (open tube, no dec); IR (KBr) 2960, 2900, 1420, 1290, 1040, 950, 860, 760 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 1.83 (d, J_{P-H} = 13.7 Hz, 18 H), 1.674 (d, J_{P-H} = 9.0 Hz, 18 H), 1.672 (dd, J_{P-H} = 24.2, 9.4 Hz, 4H); $^{13}C\{^1H\}$ NMR (126 MHz, 10% CD_3OD/D_2O) δ 16.5 (complex m), 14.2 (d, J_{P-C} = 55.5 Hz, J_{Pt-C} = 29.6 Hz), 6.4 (ddd, J_{P-C} = 97.5, 36.5, 11.1 Hz, J_{Pt-C} = 530.0 Hz); $^{31}P\{^1H\}$ NMR (146 MHz, D_2O) δ 27.94 (6-line pattern, partially obscured by ^{195}Pt satellites, J_{Pt-P} = 62.1 Hz), −26.41 (6-line pattern, J_{Pt-P} = 2253 Hz).[14] Anal. Calcd for $C_{14}H_{40}I_2P_4Pt$: C, 21.52; H, 5.16. Found: C, 21.51; H, 5.21.

(13) No ^{195}Pt satellites were resolved for the overlapping methylene and phosphine resonances in the ^1H NMR spectrum.

complete substitution by four phosphine equivalents can be effected. Efforts are currently underway to clarify the mechanism of the triphenylphosphine ylide forming reaction, to use these reactivity patterns to control related reactions in this series, and to investigate the chemistry of these interesting bis(phosphonium ylide) transition-metal complexes.

Acknowledgment. We thank Dr. Mark J. Hampden-Smith and Professor Christopher J. Samuel for helpful discussions and John C. Huffman for the X-ray crystal structure determination. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supplementary Material Available: Details of the data collection and structure solution, atomic positional and thermal parameters, and complete bond distance and angle data (16 pages); a listing of F_o vs F_c (11 pages). Ordering information is given on any current masthead page.

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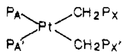
(14) The observed ^{31}P resonances (four approximately equally spaced strong lines flanked on each side by a weak line) were analyzed as an AA′XX′ spin system (^{195}Pt coupling neglected) by using the labeling scheme shown and simulated by using the observed chemical shifts and the following coupling constants:

$$J_{AA'} = 19.1\ \text{Hz}$$
$$J_{AX'} = J_{A'X} = 14.0\ \text{Hz}$$
$$J_{AX} \approx J_{A'X'} \approx J_{XX'} \approx 0\ \text{Hz}$$



Calculations were carried out on an IBM PC-XT using the program PCPMR, available through Serena Software, P.O. Box 3076, Bloomington, IN 47402.

Additions and Corrections

Ann E. Ogilvy, M. Draganjac, Thomas B. Rauchfuss,* and Scott R. Wilson: Activation and Desulfurization of Thiophene and Benzothiophene by Iron Carbonyls. **1988**, 7, 1171.

On p 1172, the last sentence in the second paragraph should cite ref 22b, not ref 21. Reference 22b should read: Hachgenei, J. W.; Angelici, R. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 909.

Book Reviews

Gmelin Handbook of Inorganic Chemistry. Eighth Edition. Cu. Organocopper Compounds. Part 4. H. Bauer, J. Faust, R. Froböse, J. Füssel, U. Krüerke, M. Kurz, and H. M. Somer, volume authors. J. Füssel, volume chief editor. Gmelin Institut für Anorganische Chemie der Max-Planck-Gesellschaft zur Förderung der Wissenschaften and Springer-Verlag, Berlin. 1987. xii + 272 pages. DM 1249.

The present book and Part 5, the index volume (244 pages, DM 1189), complete the Gmelin Handbook miniseries on organocopper compounds. In contrast to the first three volumes, Part 4 deals mostly with "real" organocopper compounds, ones which have been isolated or for which structurally useful solution data have been obtained (in contrast to the many organocopper reagents for which the only information available is method of preparation and reactivity toward organic substrates). This volume covers mononuclear organocopper compounds with ligands bonded to copper by two or more carbon atoms as well as organocopper compounds of higher nuclearity.

The explosive copper(II) acetylide is the first compound described in this book. It is followed by detailed coverage of η^2-olefin and acetylene complexes of copper, both classes of compounds that have received a good bit of attention. Mononuclear copper complexes with ligands bonded by three and more carbon atoms come next. Of these, only the η^5-cyclopentadienylcopper derivatives take up more than one or two pages.

The rest of the book (169 pages) is devoted to di- and polynuclear organocopper compounds: a few "higher-order" cuprates about whose structure in the solid state or in solution something definitive is known, some copper carbonyls, and organocopper compounds with organic or halogen bridges between two Cu atoms. The tetranuclear copper compounds are mostly of the type R_4Cu_4, R_5Cu_4Li, R_6Cu_4Mg, and $R_4Cu_4M_2X_2$, and quite a few have been characterized by X-ray diffraction.

As usual in a Gmelin Handbook volume, all available information is provided about the compounds covered. For those which are soluble in organic solvents the NMR data that have been obtained are given. If an X-ray crystal structure determination was carried out, a figure generally shows the structure. For every compound, information concerning preparation, physical properties, and reactivity are given, insofar as it is available.

It should be noted that some of the organocopper compounds listed in earlier volumes of this series very likely are polynuclear species. However, in the absence of definitive information on molecular weight and structure in solution or in the solid state, these were listed under their simplest empirical formula with the mononuclear compounds. The reader should keep this in mind when he is searching for a specific compound.

These four books bring a useful overview of organocopper compounds, and this series, while of interest to organometallic and inorganic chemists, should be of great value to the synthetic organic chemist since a detailed exposition of the applications of all kinds of organocopper reagents in organic synthesis, with a large number of examples, is provided.

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