686 (9, $Mn_2L_2^+$), 398 (23, Mn_2L^+), 343 (34, MnL^+), 55 (100, Mn^+), minor peaks at *m/e* ca. 826 ($Mn_2(CO)_5L_2^+$), 742 ($Mn_2(CO)_2L_2^+$), 714 ($Mn_2(CO)L_2^+$); peaks due to ligand dissociation were also present. Anal. Calcd for $C_{40}H_{44}O_6P_4Mn_2$: C, 56.22; H, 5.19; Mn, 12.86; P, 14.50. Found: C, 56.51; H, 5.56; Mn, 11.31; P, 13.83.

$Mn_2(CO)_5(depm)_2$. $Mn_2(CO)_{10}$ (0.43 g, 1.11 mmol) and depm (0.64 g, 2.22 mmol) were stirred in vigorously refluxing decane (65 mL) for 9.5 h. A mustard colored precipitate formed upon cooling; this solid was filtered, washed three times with pentane, and vacuum dried. TLC on silica gel with 1:1 cyclohexane–toluene as eluent indicated two spots of nearly equal intensity: one orange, R_f = 0.40, and one yellow, R_f = 0.55. The colored bands were extracted from several plates with CH_2Cl_2, and the IR spectra of the resulting solutions indicated the yellow band was $Mn_2(CO)_6(depm)_2$ and the orange band, $Mn_2(CO)_5(depm)_2$. Attempts to recrystallize the pentacarbonyl resulted in decomposition to the hexacarbonyl and intractable brown material.

$Mn_2(CO)_5(dcpm)_2$. $Mn_2(CO)_{10}$ (1.45 g, 3.72 mmol) and dcpm (2.95 g, 7.44 mmol) were combined in 120 mL of degassed decane, and this mixture was heated at reflux with stirring. After 1.25–1.75 h the solvent was removed on a rotary evaporator and the residue was dissolved in a minimum amount of benzene. This solution was passed through a 42.5 mm × 15 mm diameter Florisil chromatography column, eluting with a solution of 5:2 cyclohexane–benzene. Evaporation of the eluate and washing the resulting residue with pentane afforded 2.13 g of orange solid.

TLC on silica gel with 5:2 cyclohexane–benzene indicated at least three components. Compounds were extracted with CH_2Cl_2 from plastic backed plates by cutting up plates into segments each containing only one spot or band. IR spectra of extracted solutions indicated the presence of $Mn_2(CO)_5(dcpm)_2$, $Mn_2(CO)_6(dcpm)_2$ (the major impurity), and $HMn(CO)_3(dcpm)$. Recrystallization of the original impure product from CH_2Cl_2 and hexane by controlled evaporation in air produced bright red crystals of the pentacarbonyl. Further treatment of the recrystallization filtrate is discussed below. Anal. Calcd for $C_{55}H_{88}O_5P_4Mn_2$: C, 63.34; H, 6.57; Mn, 10.54; P, 10.88. Found: C, 63.24; H, 6.65; Mn, 9.81; P, 11.30.

$HMn(CO)_3(dcpm)$. The recrystallization solution of $Mn_2(CO)_5(dcpm)_2$ was decanted from the red crystals of this compound, and controlled evaporation of the CH_2Cl_2–hexane solvent system produced yellow crystals. Also deposited were a few large red crystals of the pentacarbonyl; these were physically separated from the yellow crystals. The IR spectrum of the yellow crystals in solution indicated no trace of pentacarbonyl VII. Anal. Calcd for $HMn(CO)_3(dcpm)\cdot CH_2Cl_2$ ($C_{29}H_{37}Cl_2O_3P_2Mn$): C, 56.05; H, 6.00. Found: C, 56.22; H, 6.38.

$Mn_2(CO)_6(dcpm)_2$. Carbonylation of an unpurified sample of $Mn_2(CO)_5(dcpm)_2$ was performed in both cyclohexane solution (0.6 g in 60 mL) and methylcyclohexane solution (1.5 g in 60 mL). In the latter case, the mixture was stirred in a 200-cm^3 Roth bomb under 3.2 MPa of CO and at 165 °C for 4 h. The solvent was removed by rotary evaporation; the residue was washed with hexane to yield an orange solid which had no impurities by IR analysis; yield 0.69 g (46%). Recrystallization in air from CH_2Cl_2 and hexane resulted in orange crystals. Anal. Calcd for $Mn_2(CO)_6(dcpm)_2\cdot CH_2Cl_2$, $C_{57}H_{70}O_6P_4Cl_2Mn_2$: C, 59.23; H, 6.10; Mn, 9.51; P, 10.72. Found: C, 58.83; H, 6.05; Mn, 9.36; P, 10.53.

Acknowledgment. We thank Dr. Hugh Huffman of the Analytical and Information Division of Exxon Research and Engineering Co. for the mass spectra. We remember and gratefully acknowledge the many stimulating and fruitful discussions with the late Dr. Rowland Pettit during the course of this work; his scientific counsel and encouragement are missed.

Registry No. V, 83291-35-4; VI, 83291-36-5; VII, 83311-75-5; VIII, 83291-37-6; IX, 83291-38-7; $Mn_2(CO)_{10}$, 10170-69-1; Mn, 7439-96-5; depm, 68861-75-6; dcpm, 83291-39-8.

Uncatalyzed and Low-Valent Nickel-Assisted Reactions of α,β-Unsaturated Aldehyde Dimethyl Acetals with Grignard Reagents[†]

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The reactions between the dimethyl acetals of acrolein, crotonaldehyde, dimethylacrolein, 1-cyclohexenecarboxaldehyde, cinnamaldehyde, and benzaldehyde with phenylmagnesium bromide and, on occasion, methylmagnesium bromide under the influence of and in the absence of bis(triphenylphophine)nickel dichloride are described. The methoxy groups are shown to be replaced by phenyl (or methyl) functions at the original carbon–oxygen bond site or a position allylic thereto, and the catalyst is shown not only to enhance the reaction rate of sterically unencumbered acetals but also to affect the regiochemistry.

In continuation of a general study of Grignard reagents with allyl alcohols under the influence of low-valent nickel catalyst,[2,3] the effect of two allylic oxy substituents in the same propene framework on the allylic carbon–oxygen bond-breaking, carbon–carbon bond-forming process became of interest. As a consequence an investigation of the behavior of α,β-unsaturated acetals in the substitution reaction was undertaken.

In view of the known displacement of at least one alkoxy function of such acetals by Grignard reagents alone,[4] the study had to be paralleled by an investigation of the uncatalyzed substitution process. Initially the dimethyl acetals of acrolein (**1a**),[5] crotonaldehyde (**1b**),[6] and di-

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[†] Dedicated to the memory of Professor R. Pettit.

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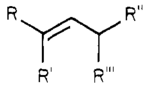
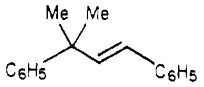
methylacrolein (**1c**)[7] were exposed to phenylmagnesium bromide in refluxing benzene solution in ca. 1:4 ratio. Acrolein dimethyl acetal (**1a**) yielded (ca. 43%) after an ca. 24-h period a mixture of 3,3-diphenyl-1-propene (**1d**),[8] 1,3-diphenyl-1-propene (**1e**),[9] and 1-methoxy-3-phenyl-1-propene (**1f**).[10] The production of these substances can be rationalized on the basis of the assumption of both magnesium ion-catalyzed methoxy group losses being accompanied by C(1) as well as C(3) phenylations. Thus the first reaction at the two sites leads to the intermediate allyl ether **1g** and enol ether product **1f**, respectively, and the subsequent replacement process, operating on intermediate **1g**, affords olefins **1d** and **1e**, respectively.[11] Crotonaldehyde dimethyl acetal (**1b**) produced (50% yield) in an ca. 24-h time period a 1:1 mixture of 1,1-diphenyl-2-butene (**1h**)[12] and 1,3-diphenyl-1-butene (**1i**).[13] Hence the presence of a 3-methyl substituent on the acrolein unit creates enough steric interference to cause the first phenylation to occur only at C(1), although the subsequent reaction on the resultant intermediate allyl ether **1j** follows both a C(1) and C(3) phenylation pathway. Finally, dimethylacrolein dimethyl acetal (**1c**) yielded (53%) 1,1-diphenyl-3-methyl-2-butene (**1k**) as sole product, indicating that the presence of two methyl groups in the starting compound precludes C(3) phenylation in either substitution step.



1a–q

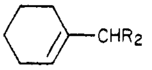
a, $R = R' = H$, $R'' = R''' = OMe$
b, $R = Me$, $R' = H$, $R'' = R''' = OMe$
c, $R = R' = Me$, $R'' = R''' = OMe$
d, $R = R' = H$, $R'' = R''' = C_6H_5$
e, $R = R'' = C_6H_5$, $R' = R''' = H$;
f, $R = OMe$, $R' = R''' = H$, $R'' = C_6H_5$
g, $R = R' = H$, $R'' = OMe$, $R''' = C_6H_5$
h, $R = Me$, $R' = H$, $R'' = R''' = C_6H_5$
i, $R = R'' = C_6H_5$, $R' = H$, $R''' = Me$
j, $R = Me$, $R' = H$, $R'' = OMe$, $R''' = C_6H_5$
k, $R = R' = Me$, $R'' = R''' = C_6H_5$
l, $R = R' = Me$, $R'' = OMe$, $R''' = C_6H_5$
m, $R = C_6H_5$, $R' = H$, $R'' = R''' = OMe$
n, $R = R'' = R''' = C_6H_5$, $R' = H$
o, $R = C_6H_5$, $R' = H$, $R'' = R''' = Me$
p, $R = R'' = Me$, $R' = H$, $R''' = C_6H_5$
q, $R = C_6H_5$, $R' = H$, $R'' = Me$, $R''' = OMe$



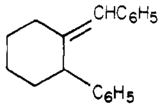
2

When the reactions were executed in the presence of bis(triphenylphosphine)nickel dichloride, the reaction rate and regiochemistry changed.[14] The reactions of the dimethyl acetals of acrolein (**1a**) and crotonaldehyde (**1b**) were complete in 6 or less hours and yielded single products, olefins **1e** (60%) and **1i** (55%), respectively. Whereas the reaction of dimethylacrolein dimethyl acetal (**1c**) was slow (24 h), in contrast to the uncatalyzed reaction it yielded (60%) two products, **1k** and 1,3-diphenyl-3-methyl-1-butene (**2**)[15] in ca. 3:1 ratio. These results are explicable most readily on grounds of the first reaction being uncatalyzed and the subsequent reaction of the intermediate 1-phenylallyl methyl ethers involving (1-phenyl-π-allyl)nickel complexes whose intramolecular phenylation takes place in such manner as to afford conjugated products exclusively.[3] Since the first methoxy group displacement of acrolein acetal (**1a**) leads not only to an allyl ether but also to enol ether **1f** (*vide supra*), the latter must undergo nickel-assisted phenylation by an alternate pathway.[16] The low rate of reaction of dimethylacrolein dimethyl acetal (**1c**) and the preponderant formation of unconjugated olefin **1k** suggest that in this case even the second reaction, i.e., the methoxy group displacement of 1-methoxy-3-methyl-1-phenyl-2-butene (**1l**) by a phenyl unit, may be mostly uncatalyzed in view of the difficulty associated with the formation of the sterically encumbered (1,1-dimethyl-3-phenyl-π-allyl)nickel complex.

Steric effects also play a role in the reaction between 1-cyclohexenecarboxaldehyde dimethyl acetal (**3a**)[17] and phenylmagnesium bromide. Both uncatalyzed and nickel-assisted reactions were slow and led to the same mixture (55–60% yield) of olefins **3b** and **4** (1.4:1 ratio), indicative of no or little (π-allyl)nickel species being formed in the latter reaction.



3a, $R = OMe$
b, $R = C_6H_5$



4

Interaction of cinnamaldehyde dimethyl acetal (**1m**)[18] with phenylmagnesium bromide in an unassisted reaction yielded (53%) a single product (**1n**)[19] in a 27-h period. Nickel catalysis produced the same styrene (77%) in shorter time (8 h). The catalysis was noticeable by both the rate and regiochemistry of the reaction of the acetal **1m** with methylmagnesium bromide. Whereas the uncatalyzed reaction led to a mixture (80% yield, 1:1 ratio) of olefins **1o**[20] and **1p**[21] in 27 h, the catalyzed process yielded (78%) only styrene **1o** in 4 h. Once again the nickel-aided reaction had followed a path leading to a conjugated product.[3] The rates of the first and second methoxy group replacements are dramatically different, permitting the introduction of two dissimilar substituents into the cinnamyl structure unit. Thus reaction of the acetal **1m** with methylmagnesium bromide for 2 h yielded (92%) cinnamyl ether **1q**,[18] whose exposure to phenylmagnesium bromide

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(11) Early quenching of the reaction revealed the presence of intermediate 3-methoxy-3-phenylpropene (**1g**) [^1H NMR ($CDCl_3$) δ 3.31 (s, 3, OMe), 4.60 (d, 1, $J = 7$ Hz, H-3), 5.1–6.1 (12-line ABX pattern, 3, H_2-1, H-2), 7.25 (s, 5, aromatic H's)].

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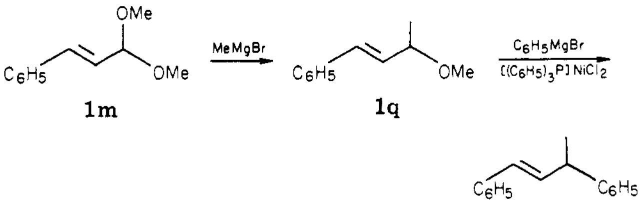
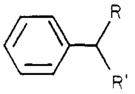
in the presence of the nickel complex produced (58%) styrene **1i**.[22]



1m **1q** **1i**

The low-valent nickel species had no effect on the rapid (2 h) conversion of benzaldehyde dimethyl acetal (**5a**)[23] into α-phenylethyl methyl ether (**5b**)[24] (80–89% yield) on interaction with methylmagnesium bromide nor on the inertness of the product toward further methylation. The inability of nickel to form complexes of the π-allyl type with benzyl groups explains the absence of catalysis. Furthermore, the cessation of the uncatalyzed reaction after the substitution of only one methoxy group is understandable on the basis of the difference of ease of the magnesium ion-catalyzed dissociation of carbon–oxygen bonds leading to transition states approximating methoxybenzyl vs. α-phenylethyl cation structures.[25]



5a, R = R' = OMe
b, R = Me, R' = OMe

Experimental Section

Melting points were determined on a Fischer-Johns apparatus and are uncorrected. Infrared spectra of thin, neat films (unless noted otherwise) were recorded on a Beckman IR 4230 spectrophotometer and ^{1}H NMR spectra of deuteriochloroform solutions with Me_4Si as internal standard (δ = 0 ppm) were obtained on a Varian EM-390 spectrometer. Analytical GC was performed on a flame ionization Varian 1200 chromatograph with columns of 80–100 mesh 5% OV 101 on Chromosorb W. Low-resolution mass spectra were recorded on a Finnigan 3300 GC–MS spectrometer (with a 6100 data system) and high-resolution mass spectra on a CEC/Du Pont 21-110B HR-MS instrument (with employment of the peak matching method).

General Procedure for the Reactions of Phenylmagnesium Bromide. An ethereal solution of phenylmagnesium bromide, 8.0 mL (20.0 mmol) of 2.5 M, was poured into 10 mL of dry benzene and most of the ether removed by distillation. Upon the addition of 5.0 mmol of acetal the solution was refluxed under argon.[26] Thereafter the cooled mixture was poured into an aqueous, saturated ammonium chloride solution and extracted with ether. Drying the extract over Na_2SO_4 and evaporation yielded the product.

An ethereal solution of methylmagnesium bromide, 0.4 mL (1.0 mmol) of 2.5 M, was poured into a solution of 320 mg (0.5 mmol) of bis(triphenylphosphine)nickel dichloride in 10 mL of dry benzene and the mixture stirred at room temperature for 15 min. Thereupon an ethereal solution of phenylmagnesium bromide, 8.0 mL (20 mmol) of 2.5 M, was added and most of the ether removed by distillation. Acetal, 5.0 mmol, was added and the solution refluxed under argon.[26] Workup as above yielded the product.

Reactions with Acrolein Dimethyl Acetal (1a). An uncatalyzed reaction for 24 h, chromatography of the crude product on basic alumina (activity I), and elution with hexane gave some biphenyl, a 13% yield of liquid 3,3-diphenyl-1-propene (**1d**)[8] [IR C=C 1600 (m) cm^{-1}; ^{1}H NMR δ 4.70 (d, 1, J = 6 Hz, CH), 4.8–5.3, 6.1–6.5 (12-line m, 3, vinyl H's), 7.1–7.7 (m, 10, aromatic H's)], a nd a 20% yield of liquid 1,3-diphenyl-1-propene (**1e**)[9] [IR C=C 1605 (m) cm^{-1}; ^{1}H NMR δ 3.50 (d, 2, J = 6 Hz, CH_2), 6.2–6.4 (m, 2, olefinic H's), 7.0–7.4 (m, 10, aromatic H's). Elution with 10:1 hexane–benzene led to a 10% yield of liquid *trans*-1-methoxy-3-phenyl-1-propene (**1f**):[10] IR C=C 1655 (s) cm^{-1}; ^{1}H NMR δ 3.25 (d, 2, J = 6 Hz, CH_2), 3.49 (s, 1, Me), 4.7–5.1 (dt, 1, J = 12, 6 Hz, olefinic H), 6.35 (d, 1, J = 12 Hz, OCH), 7.20 (br s, 5, aromatic H's); spectrally identical with an authentic sample prepared by the procedure in ref 4.

A catalyzed reaction for 5 h, chromatography on silica gel impregnated with 15% silver nitrate, and elution with hexane gave a 60% yield of liquid **1e**,[9] spectrally identical with the above sample.

Reactions with Crotonaldehyde Dimethyl Acetal (1b). An uncatalyzed reaction for 24 h, chromatography on silica gel impregnated with 15% silver nitrate, and elution with hexane gave a 25% yield of liquid 1,1-diphenyl-2(*E*)-butene (**4h**)[12] [^{1}H NMR δ 1.70 (d, 3, J = 6 Hz, Me), 4.62 (d, 1, J = 6 Hz, CH), 5.39 (dq, 1, J = 10, 6 Hz, H-3), 5.90 (dd, 1, J = 10, 6 Hz, H-2), 7.1–7.4 (m, 10, aromatic H's); mass spectrum, *m/e* 208 (M$^+$, 67%), 193 (94), 130 (49), 115 (base), 91 (73)] and a 25% yield of liquid 1,3-diphenyl-1(*E*)-butene (**1i**)[13] [IR C=C 1605 (w) cm^{-1}; ^{1}H NMR δ 1.43 (d, 3, J = 6 Hz, Me), 3.4–3.8 (m, 1, CH), 6.3 (m, 2, olefinic H's), 7.0–7.4 (m, 10, aromatic H's)].

A catalyzed reaction was over in 6 h. The same chromatography and elution gave a 55% yield of liquid **1i**,[13] spectrally identical with the above sample.

Reactions with Dimethylacrolein Dimethyl Acetal (1c). An uncatalyzed reaction for 24 h, chromatography on basic alumina (activity I), and elution with hexane afforded a 53% yield of liquid 1,1-diphenyl-3-methyl-2-butene (**1k**): IR C=C 1600 (m) cm^{-1}; ^{1}H NMR δ 1.69, 1.78 (s, 3 each, Me), 4.85 (d, 1, J = 9 Hz, CH), 5.61 (d, 1, J = 9 Hz, olefinic H), 7.11 (s, 10, aromatic H's); mass spectrum, *m/e* 222 (M$^+$, 32%), 207 (41), 129 (base), 91 (68); exact mass *m/e* 222.1412 (calcd for $C_{17}H_{18}$ *m/e* 222.1409).

A catalyzed reaction for 24 h and the same chromatographic workup led to **1k** (spectrally identical with the above sample) in 42% yield and liquid 1,3-diphenyl-3-methyl-1-butene (**2**)[15] (18% yield): ^{1}H NMR δ 1.43 (s, 6, Me_2), 6.32 (s, 2, olefinic H's), 7.1–7.5 (m, 10, aromatic H's); mass spectrum, *m/e* 222 (M$^+$, 87%), 207 (77), 178 (70), 144 (89), 130 (98), 128 (99), 92 (base).

Reactions with 1-Cyclohexenecarboxaldehyde Dimethyl Acetal (3a). An uncatalyzed reaction for 24 h, chromatography on basic alumina (activity I), and elution with hexane gave a 32% yield of liquid (1-cyclohexenyl)diphenylmethane (**3b**): IR C=C 1660 (m), 1650 (w) cm^{-1}; ^{1}H NMR δ 1.4–2.2 (m, 8, methylenes), 4.58 (s, 1, CH), 5.19 (br s, 1, olefinic H), 7.0–7.3 (m, 10, aromatic H's); mass spectrum, *m/e* 248 (M$^+$, base), 205 (30%), 167 (78), 91 (35); exact mass *m/e* 248.1563 (calcd for $C_{19}H_{20}$ *m/e* 248.1565).

Further elution with hexane yielded liquid 1-benzylidene-2-phenylcyclohexane (**4**; 23%) (in the form of a single isomer of unknown stereochemistry): IR C=C 1660 (m), 1640 (w) cm^{-1}; ^{1}H NMR δ 1.5–2.9 (m, 8 methylenes), 3.41 (t, 1, J = 6 Hz, CH), 5.75 (s, 1, olefinic H), 7.0–7.3 (m, 10, aromatic H's); mass spectrum, *m/e* 248 (M$^+$, 48%), 157 (43), 129 (76), 115 (80), 91 (base); exact mass: *m/e* 248.1563 (calcd for $C_{19}H_{20}$ *m/e* 248.1565).

The catalyzed reaction led in 24 h to compounds **3b** and **4** in 35 and 25% yields, respectively.

Reactions with Cinnamaldehyde Dimethyl Acetal (1m). An uncatalyzed reaction for 27 h and workup only with water led to a 53% yield of liquid 1,3,3-triphenyl-1(*E*)-propene (**1n**):[19] IR C=C 1655 (w), 1600 (w) cm^{-1}; ^{1}H NMR δ 4.85 (d, 1, J = 6 Hz, CH), 6.30 (d, 1, J = 12 Hz, olefinic H), 6.70 (dd, 1, J = 12, 6 Hz, olefinic H), 7.1–7.4 (m, 15, aromatic H's). Workup with saturated ammonium chloride solution and/or chromatography over basic alumina (activity I) converted the product into its isomer 1,1,3-triphenyl-1-propene (1, R = R' = R'' = C_6H_5, R''' = H);[24] IR C=C 1660 (w), 1597 (m) cm^{-1}; ^{1}H NMR δ 3.42 (d, 2, J = 7 Hz, CH_2),

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[25] All Grignard reactions led to stereochemically unique olefins, whose configuration, unknown for olefins **1e,o,p** and **2**, is described in the Experimental Section.

[26] The Grignard reagent/acetal ratio could be dropped to nearly 1:1 without undue effect on the product yield.

6.22 (t, 1, J = 7 Hz, olefinic H), 7.1–7.4 (m, 15, aromatic H's); mass spectrum, m/e 270 (M^+, 8%), 192 (65), 179 (40), 178 (42), 165 (43), 115 (93), 91 (base).

The catalyzed reaction afforded a 77% yield of **1n** in 8 h reaction time.

1,3-Diphenyl-1(*E*)-butene (1i). A catalyzed reaction with 3-methoxy-1-phenyl-1-butene (**1q**) (vide infra) for 5 h, chromatography on silica gel impregnated with 15% silver nitrate, and elution with hexane led to a 58% yield of oily styrene **1i**:[22] ^{1}H NMR δ 1.40 (d, 3, J = 6 Hz, Me), 3.60 (m, 1, CH), 6.2–6.4 (m, 2, olefinic H's), 7.0–7.3 (m, 10, aromatic H's).

General Procedure for the Reactions of Methylmagnesium Bromide. An ethereal solution of methylmagnesium bromide, 7 mL (17.5 mmol) of 2.5 M, was poured into 10 mL of dry benzene and most of the ether removed by distillation. The acetal, 5.0 mmol, was added and the mixture refluxed under argon. Upon conclusion of the reaction the mixture was worked up as in the above Grignard reactions.

An ethereal solution of methylmagnesium bromide, 7 mL (17.5 mmol) of 2.5 M, was poured into a solution of 320 mg (0.5 mmol) of bis(triphenylphosphine)nickel dichloride in 10 mL of dry benzene, the mixture stirred at room temperature for 15 min, and most of the ether removed by distillation. The acetal, 5.0 mmol, was added and the mixture refluxed under argon.[26] Workup as before yielded the product.

Reactions with Cinnamaldehyde Dimethyl Acetal (1m). An uncatalyzed reaction for 27 h, chromatography on silica gel impregnated with 15% silver nitrate, and elution with hexane led to liquid 3-methyl-1-phenyl-1-butene (**1o**)[20] (40% yield): IR C=C 1610 (w) cm^{-1}; ^{1}H NMR δ 1.03 (d, 6, J = 6 Hz, Me_2), 2.40 (5-line m, 1, J = 6 Hz, CH), 6.1–6.3 (m, 2, olefinic H's), 7.1–7.4 (m, 5, aromatic H's). Further elution gave liquid 4-phenyl-2-pentene (**1p**)[21] (40% yield): IR C=C 1600 (w) cm^{-1}; ^{1}H NMR δ 1.32 (d, 3, J = 6 Hz, Me), 1.59 (d, 3, J = 6 Hz, olefinic Me), 3.3–3.6 (m, 1, CH), 5.4–5.7 (m, 2, olefinic H's), 7.20 (s, 5, aromatic H's).

The catalyzed reaction for 4 h, chromatography on basic alumina (activity I), and elution with hexane gave **1o**[20] in 78% yield.

An ethereal solution of methylmagnesium bromide, 4 mL (6 mmol) of 1.5 M, was added to 10 mL of dry benzene and most of the ether removed by distillation. Acetal, 5 mmol, was added and the mixture refluxed for 2 h. The usual workup, chromatography on basic alumina (activity I), and elution with hexane led to a 92% yield of liquid 3-methoxy-1-phenyl-1(*E*)-butene (**1q**):[18] IR C=C 1600 (w) cm^{-1}; ^{1}H NMR δ 1.31 (d, 3, J = 6 Hz, Me), 3.28 (s, 3, OMe), 3.85 (5-line m, 1, J = 6 Hz, CH), 6.02 (dd, 1, J = 13, 6 Hz, H-2), 6.48 (d, 1, J = 13 Hz, H-1), 7.1–7.4 (m, 5, aromatic H's).

Reactions with Benzaldehyde Dimethyl Acetal (5a). The uncatalyzed reaction for 2 h, chromatography on basic alumina (activity I), and elution with hexane afforded an 89% yield of liquid α-phenylethyl methyl ether (**5b**):[24] ^{1}H NMR δ 1.39 (d, 3, J = 6 Hz, Me), 3.18 (s, 3, OMe), 4.25 (q, 1, J = 6 Hz, CH), 7.30 (s, 5, aromatic H's).

The catalyzed reaction also lasted 2 h. Its workup as above led to an 80% yield of **5b**.[24]

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Registry No. **1a**, 6044-68-4; (*E*)-**1b**, 18318-79-1; **1c**, 31525-65-2; **1d**, 3542-14-1; (*E*)-**1e**, 3412-44-0; (*E*)-**1f**, 60053-38-5; **1g**, 22665-13-0; (*E*)-**1h**, 4416-96-0; (*E*)-**1i**, 7302-01-4; (*E*)-**1j**, 83605-30-5; **1k**, 51507-36-9; **1l**, 83605-31-6; (*E*)-**1m**, 63511-93-3; (*E*)-**1n**, 18916-14-8; (*E*)-**1o**, 15325-61-8; (*E*)-**1p**, 42461-65-4; (*E*)-**1q**, 24808-74-0; (*E*)-**2**, 56763-59-8; **3a**, 61967-21-3; **3b**, 83605-32-7; **4**, 83605-33-8; **5a**, 1125-88-8; **5b**, 4013-34-7; bis(triphenylphosphine)nickel dichloride, 14264-16-5; phenyl bromide, 108-86-1; methyl bromide, 74-83-9.

Transition Metal Methylene Complexes. 36.[1] Chelate-Type Bridging α-Diazo Ketones through Cleavage of a Metal–Metal Triple Bond[†]

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Cleavage of the metal–metal triple bond of bis[dicarbonyl(η^5-pentamethylcyclopentadienyl)molybdenum](*Mo≡Mo*) (**1a**) is effected by the α-ketodiazoalkanes **2a–d** resulting in the formation of the chelate-type dinuclear insertion products **3a–d**. An X-ray crystallographic study of the key compound **3a** revealed the central structural frame $\mathrm{Mo{=}N\overline{NC(R){=}C(CH_3)OMo}}$ [R = C(=O)CH_3] to be composed of an essentially planar five-membered metallacyclic unit that coordinates to the second metal atom via a terminal nitrogen group (Mo(2)–N(2) = 183.6 (17) pm; N(1)–N(2) = 124.4 (24) pm). No molybdenum–molybdenum bond is present after α-diazo ketone addition to the unsaturated organometallic precursor **1a**, with the nonbonding MoMo distance being longer than 380 pm. Metal–metal bond cleavage appears to be prevalent in the reactions of metal–metal triple bonds with carbonyl-flanked diazoalkanes capable of chelating mononuclear organometallic fragments.

Introduction

Organometallic compounds having metal–metal double bonds offer a straightforward route to μ-alkylidene complexes of type $\mathrm{L_x\overline{MCRR'M}L_x}$ when treated with various diazoalkanes.[4–6] These reactions normally proceed rapidly even under very mild conditions, and not one case is known in which intermediates containing the intact diazo pre-

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[†] In memoriam of Rowland Pettit.

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