sulting material was dissolved in a minimal amount of chloroform. The solution was cooled to 0 °C and filtered. The organic solution was evaporated, and the residue was taken up in ether. The ether solution was extracted with 20% potassium bicarbonate (3 × 100 mL). The resulting aqueous solution was acidified and extracted with ether (3 × 100 mL). The ether solution was dried over anhydrous sodium sulfate, and the solvent was removed. The residue was then chromatographed on 70–230-mesh silica gel by eluting with 5% methanol in chloroform to give 2.52 g (83%) of product: ^{1}H NMR ($CDCl_3$) δ 0.8–1.1 (m, 3 H), 1.1–1.5 (m, 8 H), 1.5–1.85 (m, 2 H), 2.6–2.8 (m, 4 H), 3.63 (t, 2 H), 4.9 (s, 2 H), 7.4 (s, 5 H); HRMS calcd for $C_{18}H_{27}NO_4$ 321.1938, found 321.1952.

***N*-[5-[3-[Heptyl(benzyloxy)carbamoyl]propionamido]-pentyl]-3-[[5-[(benzyloxy)acetylamino]pentyl]carbamoyl]-*O*-benzylpropionohydroxamic Acid (5a).** The acid **3a** (0.749 g, 2.3 mmol) and **7** (1.11 g, 2.1 mmol) were dissolved in 11 mL of anhydrous dichloromethane. To this were added 0.6 g (2.9 mmol) of dicyclohexylcarbodiimide and 32 mg (0.26 mmol) of (dimethylamino)pyridine, and the solution was stirred at room temperature for 20 h. The reaction mixture was cooled to 0 °C and filtered. The solvent was removed, and the crude material was purified by chromatography on 70–230-mesh silica gel by eluting with 2% methanol in chloroform to give 1.3 g (73%) of product: ^{1}H NMR ($CDCl_3$) δ 0.70–1.05 (m, 3 H), 1.05–1.9 (m, 22 H), 2.1 (s, 3 H), 2.25–2.64 (m, 4 H), 2.64–3.0 (m, 4 H), 3.0–3.4 (m, 4 H), 3.5–3.8 (m, 6 H), 4.83 (s, 2 H), 4.87 (s, 4 H), 6.2–6.5 (m, 2 H), 7.4 (s, 15 H); FABMS calcd for $C_{48}H_{69}N_5O_8$: 843, found 843.

***N*-[5-[3-[Heptylhydroxycarbamoyl]propionamido]-pentyl]-3-[[5-(acetylhydroxyamino)pentyl]carbamoyl]-propionohydroxamic Acid (6a).** The acid **5a** (0.49 g, 0.58 mmol) was dissolved in 8.5 mL of methanol, and 50 mg of 10% Pd/C was added. The hydrogenation was carried out overnight at 1 atm of hydrogen, the reaction mixture was filtered, and the solid was washed with hot methanol. Evaporation of the methanol gave 0.284 g (85%) of product: ^{1}H NMR (DMF-d_7) δ 0.64–0.9 (m, 3 H), 0.9–1.7 (m, 22 H), 2.0 (s, 3 H), 2.2–2.5 (m, 4 H), 2.6–2.8 (m, 4 H), 2.9–3.2 (m, 4 H), 3.3–3.6 (m, 6 H), 9.7–9.95 (m, 3 H); FABMS calcd for $C_{27}H_{51}N_5O_8$: 573, found 574 (M + 1).

Registry No. **1**, 3350-74-1; **2**, 112139-59-0; **2a**, 112151-61-8; **3**, 112139-60-3; **3a**, 112139-66-9; **4**, 112139-61-4; **5**, 112139-62-5; **5a**, 112139-67-0; **6**, 112139-63-6; **6a**, 112139-68-1; **7**, 112139-64-7; **8**, 112139-65-8; **9**, 1950-39-6; *O*-benzylhydroxylamine hydrochloride, 2687-43-6; heptanal, 111-71-7.

Main Group Conjugated Organic Anion Chemistry. 3.[1] Application of Magnesium–Anthracene Compounds in the Synthesis of Grignard Reagents

Stephen Harvey, Peter C. Junk, Colin L. Raston,*,† and Geoffrey Salem

School of Chemistry, The University of Western Australia, Nedlands 6009, Australia

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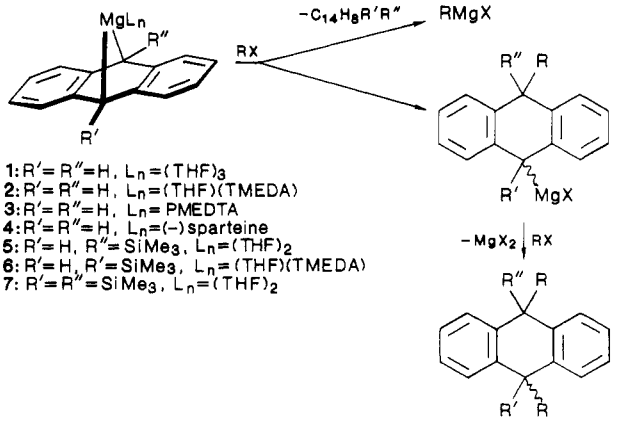
Reaction of magnesium–arene compounds, [Mg(anthracene)(THF)$_3$], **1**, and some silylanthracene, and/or tertiary amine analogues, with benzylic and allylic chlorides or bromides, and $(Me_3Si)_3CCl$, afford Grignard reagents, RMgX, in modest to high yield for chlorides and negligible to high yield for the bromides, in THF, toluene, and hexane at −10 to 20 °C. Novel benzylic-type Grignard reagents prepared in high yield include those of 9-(chloromethyl)anthracene, 2-(chloromethyl)pyridine and 8-(chloro(or bromo)methyl)quinoline, and poly-Grignard reagents derived from 1,8-bis(chloromethyl)naphthalene, 2,2′-bis(chloromethyl)-1,1′-binaphthyl, and 1,3,5-tris-(chloro(or bromo)methyl)benzene. Grignard reagent formation occurs via electron-transfer reactions. Aryl and alkyl halides yield mainly products derived from addition of the halide across the 9,10-positions of the anthracenes, via nucleophilic substitution or collapse of a diradical cage [Mg^{2+}, (anthracene)$^{\bullet-}$, $RX^{\bullet-}$.]

Introduction

Magnesium reacts with conjugated organic compounds such as polyenes, e.g. butadienes,[2,3] cyclooctatetraene[4,5] and fluoranthrene,[5] and fused aromatic compounds, e.g. anthracenes,[5-10] and isoelectronic phenazine,[1] and naphthalene,[11] in strongly coordinating solvents yielding radical anion and/or dianion species. One of the most studied is [Mg(anthracene)(THF)$_3$], **1**,[5-10,12-14] which has remarkable properties. It can act as a soluble source of magnesium, e.g. formation of MgH_2 in the presence of hydrogen,[12] or as a dinucleophile, e.g. formation of 9,10-dihydroanthracene on protonolysis.[8,12] Moreover, in some solvents it decomposes to its constituents, via Mg(anthracene)-(THF)$_2$ in benzene and toluene, and in others THF replacement prevails, e.g. with TMEDA (*N,N,N′,N′*-tetramethylethylenediamine), PMDETA (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine), and (−)-sparteine,[5] resulting in compounds of higher stability in solvents other than THF. We find that **1** acts as a source of magnesium

Scheme I



with benzylic and allylic halides and $(Me_3Si)_3CCl$, affording Grignard reagents, whereas with other halides addition

† Present address: School of Science, Griffith University, Nathan, Queensland 4111, Australia.

(1) Part 2: Junk, P. C.; Raston, C. L. Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1162.

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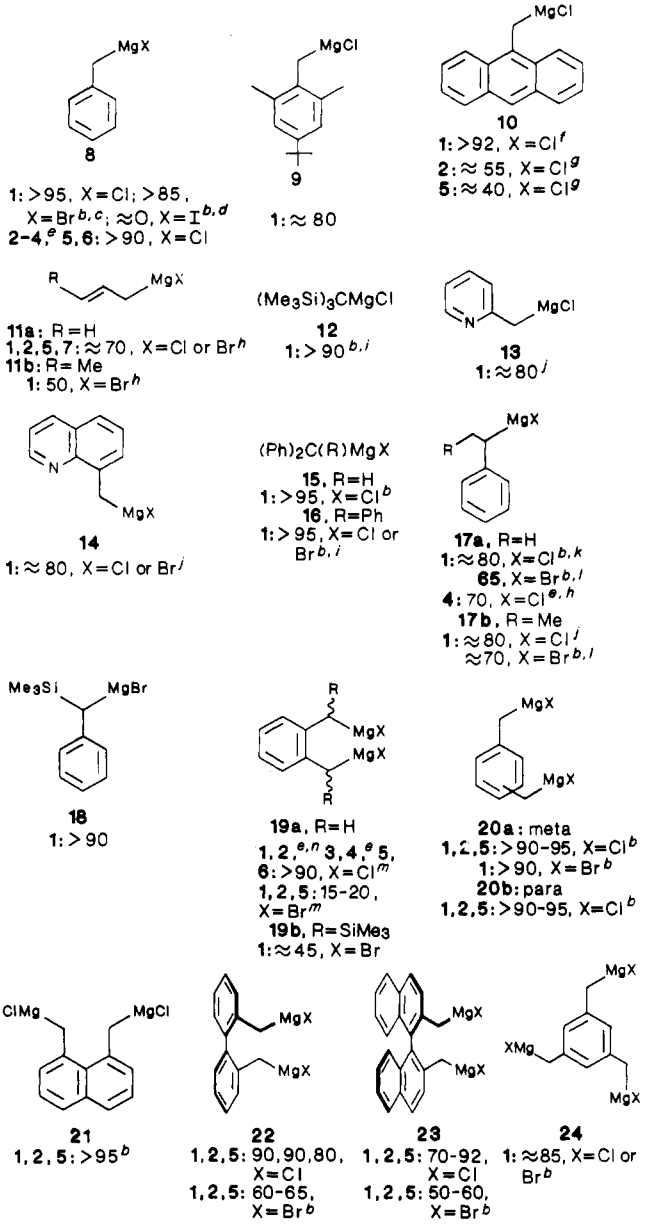
predominates, viz. 1 acts as a nucleophile, Scheme I. The results are reported herein, together with reactions for compounds with different coligands on the metal centers, **2–4**, and anthracene substitution, **5–7**, the syntheses of which are detailed in part 1[5] of the present series and in contributions from other research groups.[9]

Benzylic and allylic type Grignard reagents can be difficult to prepare or inaccessible by using the classical method of formation, viz. the treatment of magnesium powder or turnings with an organic halide, usually in a coordinating solvent.[2,3] This is in part owing to the stability of the benzylic or allylic centered radicals ($R^{\bullet}$ or $RX^{\bullet-}$), allowing departure from the metal surface and thus greater probability of forming the Wurtz-coupled product and/or the higher reactivity of the organic halide toward the preformed Grignard reagent. These side reactions can be restricted by using highly activated magnesium, generated by alkali-metal reduction of magnesium salts,[15] reversible formation of **1** with magnesium and a catalytic amount of anthracene,[8,16] or condensation of metal vapor.[17] A soluble source of magnesium, namely, **1** (ca. 3 g dm^{-3} in THF at 25 °C),[8] would in principle further restrict coupling. Furthermore, increasing its solubility, which we achieve by incorporating lipophilic trimethylsilyl groups at the C9/C10 positions of anthracene (solubility of **7** ca. 50 g dm^{-3} at 25 °C) should also restrict coupling, and steric buttressing may disfavor addition, Scheme I.

We have published a preliminary account of the reaction of **1** with a few benzylic halides[18] and details of the synthesis of a metallacycle from one of the derived Grignard reagents.[19] The only other magnesium–arene compound used for cleavage of carbon heteroatom bonds is Mg(naphthalene)$_2$, effective in ring opening of epoxides.[20]

Table I. Grignard Reagents Prepared by Treating [Mg(anthracene)(THF)$_3$], 1, or Related Magnesium–Arene Compounds 2–7 with Organic Halides in THF[a] at 20 °C (Details for Each Entry Are Percentage Yield(s) for the Magnesium–Arene Compound(s) Studied.)



[a] For simplicity no THF complexed to magnesium is shown and in all cases the nature of the Grignard species present is unknown. [b] Reaction at 0 °C. [c] 8% coupled product. [d] 100% coupled product. [e] Reaction in toluene. [f] Acid-quenched yield; 73% 9-[(trimethylsilyl)methyl]anthracene and 27% 9-methylanthracene on treatment with $ClSiMe_3$. [g] Reactions incomplete after ca. 36 h; products on quenching with $ClSiMe_3$ were 40% **2** or 55% **5** and 9-methylanthracene. [h] Isolated yield of carboxylic acid. [i] DCl/D_2O quenched to establish the yield. [j] Isolated yield of $ClSiMe_3$ derivative. [k] 18% addition product. [l] 25–35% coupled product. [m] Reaction at −10 °C. [n] Reaction in hexane.

Results and Discussion

General Considerations. Grignard reagents prepared by using **1–7**, Scheme I, are shown in Table I. Most of the reagents are new and/or at best accessible by using the classical method under rather critical conditions, **16** excepted. A typical experiment involved the slow addition of a THF solution of the organic halide to a stoichiometric

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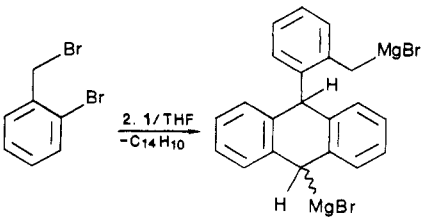
amount of the magnesium compound as a slurry in THF usually at 0 or ca. 20 °C and with a target concentration of poly-Grignard reagent close to 0.1 mol dm^{-3}. In all cases, immediately after addition of the first few drops of halide, the solution turned from bright orange, compound **1**, or yellow, compounds **2–7**, to deep green which persisted until all of the magnesium compound was consumed and addition of halide complete whereupon the solution became colorless or pale red/brown, except for **10**, **16**, and **23**. (Here solutions of the Grignard reagents are deep red.) Discharge of the green color is a reliable guide to completion of Grignard reagent formation and is an attraction of using this method. Moreover, it is a guide as to whether Wurtz coupling prevails since such coupling would require more than the stoichiometric amount of halide. The green solutions contain paramagnetic species, g_{av} close to 2.0030 with no hyperfine coupling, and presumably are the radical anions of the various anthracenes; the lack of hyperfine coupling could arise from rapid electron transfer between radical anions and "preformed anthracene". The presence of radicals implies that electron-transfer reactions prevail (see below). The choice of metal–arene compound has little effect on the overall yield of the Grignard reagent.

Grignard formation was rapid and complete within ca. 1 h, except for **10** which took 36 h to complete. The target concentration of ca. 0.1 mol dm^{-3} was chosen as a compromise between practicality and a sufficiently high dilution to disfavor Wurtz coupling. The same concentration was found to be appropriate for similar studies on the synthesis of some benzylic Grignard reagents, **19a**, R = H, X = Cl,[21] **20**, X = Cl,[22,23] and **22**, X = Cl,[24] using the classical method, albeit under rather critical conditions. The choice of reaction temperature was based on minimizing Wurtz coupling by operating at low temperature, e.g., −10 °C for **19a**, yet not low enough to stop the reaction. Highly activated magnesium, in contrast, reacts with organic halides at lower temperatures, e.g., with allylic halides at −65 °C.[16c]

A variety of procedures were employed to establish yields of Grignard reagents. These included quenching aliquots with 0.1 mol dm^{-3} HCl and back titrating with 0.1 mol dm^{-3} NaOH, ^1H NMR and GC/MS analysis of the water- or acid-quenched reaction mixtures, usually coupled with synthesis of the trimethylsilyl derivatives (via addition of $ClSiMe_3$), and isolation of carboxylation products. Where only one method was used, this is specified in Table I.

Except for **12** the Grignard reagents in Table I are derived from benzylic or allylic halides, either bromides and/or more effectively chlorides. Reactions involving other types of organic halides, however, either gave exclusively Wurtz-coupled product, e.g., benzyl iodide, failed to react, e.g., chlorobenzene and 1,2-difluorobenzene, or gave predominantly addition product(s), Scheme I. The latter was found for bromobenzene, vinyl bromide, 1-bromopropane, isopropyl bromide, *tert*-butyl chloride or bromide, 1-bromopentane, and 1-bromoadamantane. It is noteworthy that where addition prevails the solutions become red or dark brown (see above) throughout the reaction which suggests that the mechanism does not involve electron transfer as the primary process, viz. a nucleophilic substitution reaction. This is one of two common reaction pathways for organic halides with organomagnesium reagents,[25] the other being electron transfer. Addition is not by attack of preformed Grignard reagent on anthracene, since, for example, 1-pentylmagnesium bromide did not react with anthracene in THF over a period of ca. 12 h (see below). The in situ reaction of magnesium and *o*-bromofluorobenzene with anthracene in THF is thought to proceed via benzyne addition to anthracene.[26] In view of the ability of magnesium and anthracene to form **1** in THF, however, this reaction may well proceed via addition involving the bromo group followed by intramolecular coupling and elimination of magnesium halide, Scheme I.

Itsuno et al. claim that bromo-, (bromoethyl)-, and (bromopropyl)polystyrene with **1** give satisfactory yields of the corresponding Grignard reagents.[13] This is not consistent with our findings for aryl and alkyl bromides and also with a recent article on the reaction of **1** with 2 molar equiv of ethyl bromide.[14] The product is exclusively 9,10-diethyl-9,10-dihydroanthracene, Scheme I. In addition, Bickelhaupt et al. claim that our method of Grignard synthesis involving **1**, when applied to *o*-$BrC_6H_4CH_2Br$, yields the di-Grignard reagent.[27] In our hands this reaction yields a complex mixture containing ca. 25% mono-Grignard reagent derived from oxidative addition of magnesium to the benzylic–bromine bond and 25% of the addition product of the aryl bromide of this Grignard reagent, eq 1.[28a] The Grignard reagent of chloromethylated polystyrene is accessible by using **1**[13,28b] in accordance with our apparent general success of preparing Grignard reagents of benzylic chlorides.



(1)

Alkali-metal–arene$^{\bullet-}$ compounds are effective in the synthesis of a variety of organometallic compounds from organic halides, although not for allylic or benzylic halides.[29] Competing reactions are addition to the arene and Wurtz coupling.[30] Thus, like **1–7**, the metal–arene compounds behave as sources of metal or undergo nucleophilic substitution with organic halides. Magnesium–1,3-diene[2] type compounds, which are related to **1–7**, exclusively undergo substitution, although they can act as sources of metal with other substrates, e.g., I_2, yielding MgI_2,[31] and Mg(cyclooctatetraene)$(THF)_{2.5}$ discussed in part 1[5] yields the Wurtz-coupled product with benzyl chloride in THF

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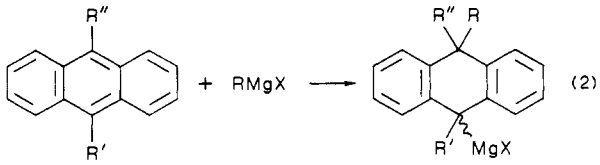
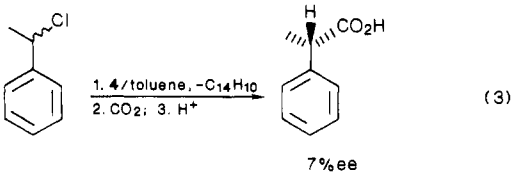
at ca. 20 °C. A secondary reaction has been identified in certain reactions of compounds 1–7, viz. the addition of preformed Grignard reagent with the generated anthracene, eq 2. These will be discussed in detail below.



(2)

THF is second to diethyl ether in its use as a solvent for Grignard reagent syntheses using the classical method for which a coordinating solvent is mandatory unless using magnesium vapors.[2,3] We find that the magnesium–arene compounds are effective in forming Grignard reagents in noncoordinating solvents, e.g., **19a**, R = H, X = Cl, from **2** in hexane or toluene, or **4** in toluene and **8**, X = Cl, from **4** in toluene, although, the coligands on the metal in these compounds would presumably satisfy the coordination requirements of the metal in the generated Grignard reagents.

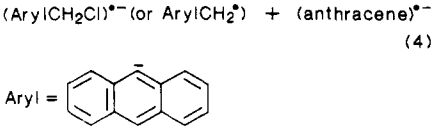
Individual Grignard Reagents. Mg(anthracene)-((−)-sparteine), **4**, was developed as a possible source of optically active magnesium. The tertiary amine is rapidly displaced in THF so reactions were carried out in toluene.[5] With (±)-methylphenylmethyl chloride ca. 7% ee was evident in the carboxylated material, eq 3, showing some asymmetric induction either during Grignard reagent formation or after via equilibration of the two diastereomers of **17a**, R = H, X = Cl.



(3)

7% ee

Reagent **10** is atypical in the time required for Grignard formation, 36 h for >92% yield using **1**; other metal–arene compounds are slower to react. Some 9-methylanthracene is formed which presumably arises from H-abstraction from the solvent and is a common type of reaction involving alkali-metal–arene compounds.[29,30] The similarity of the aryl group in the organic halide with anthracene may mean that electron transfer from 1 to RX, eq 4, is delicately



(4)

balanced. Use of excess **1**, ca. 2 molar equiv, had no effect on the rate of formation of **10**, although all of **1** was converted to a metal–(anthracene)$^{\bullet-}$ compound. The presence of a silyl group in **5** would tend to stabilize charge by polarization and disfavor electron transfer to RX and would account for its slower reaction, e.g., 50% unreacted after ca. 36 h. Reagent **10** is an implied intermediate in the in situ trapping reaction with $ClSiMe_3$, where the conditions are critical since further reaction between the 9-[(trimethylsilyl)methyl]anthracene generated and magnesium is possible.[32] No Grignard reagent formation was evident for the reaction of 9-(bromomethyl)anthracene with **1**.

Allylic halides appear to be at the threshold between forming Grignard reagents and addition products, ca. 50–70% and 30–50%, respectively. Compounds **11a** and **11b** do not add appreciably to anthracene so that addition in this case is a primary process, Scheme I, rather than secondary, eq 2. For these halides there appears to be no advantage in choice of halide, Cl^- vs Br^-, and no advantage of the present method over the use of highly activated metal.[16c]

Tris(trimethylsilyl)methyl chloride is the only non-benzylic or non-allylic halide to afford a significant amount of Grignard reagent, **14**; addition, Scheme I, is most likely sterically unfavorable. The same reagent is not formed by using magnesium metal, presumably because steric congestion about the halogen blocks electron transfer from the metal surface. In contrast, the less hindered bis(trimethylsilyl)methyl chloride readily gives a Grignard reagent using magnesium metal but gives addition, Scheme I, as well as many other ill-defined products using **1**.[33]

Benzhydrylmagnesium chloride, **15**, forms in high yield; the classical method gives negligible Grignard reagent in THF or 70% in diethyl ether.[34] The related well-known reagent **16** is accessible in high yield by using **1** and magnesium.[34] As in the classical method all of the halide is converted to $Ph_3C^{\bullet}$ prior to Grignard reagent formation (the ESR spectrum is similar to that observed for the same radical in other solvents).[35] Interestingly, both methods give red solutions containing paramagnetic species, possibly the radical anion of the Gomberg dimer, $Ph_2CC_6H_5CPh_3$,[36] and this is discussed elsewhere.[37]

Yields of secondary benzylic Grignard reagents using **1** and **4** are modest, ca. 80% for chlorides and 70% for bromides, either for a methyl or ethyl group attached to the ipso carbon, **17**. Here the competing reaction is addition, Scheme I, ca. 18%, X = Cl, 3%, X = Br, and coupling, ca. 25%, X = Br, which is the competing reaction in the classical reaction where the chloride is preferred.[38] Grignard reagent **17a**, X = Br, has been prepared via hydromagnesiation of styrene.[39] Trimethylsilyl substitution at the ipso carbon similarly results in a high yield of Grignard reagent even for the bromide, **18**, which is also accessible by using the classical reaction.[40] The di-Grignard reagent **19** was prepared from an inseparable mixture of diastereomers of the corresponding dibromide.

We now turn to features of the poly-Grignard reagent syntheses. Reaction of 1,2-bis(halogeno)methylbenzene with **1** nicely illustrates the effect of temperature and choice of halide using magnesium anthracene complexes. At ca. −10, 0, and 20 °C the amount of di-Grignard reagent formed from the dichloride is >90%, 87%, and 80%, respectively, the competing reaction being coupling and then formation of the di-Grignard reagent, **25**. At ca. 20 °C the dibromide yields 17% of the immediate di-Grignard reagent, 66% of **25**, and 6% of the next highest coupled product, **26**. The extent of coupling is not significantly

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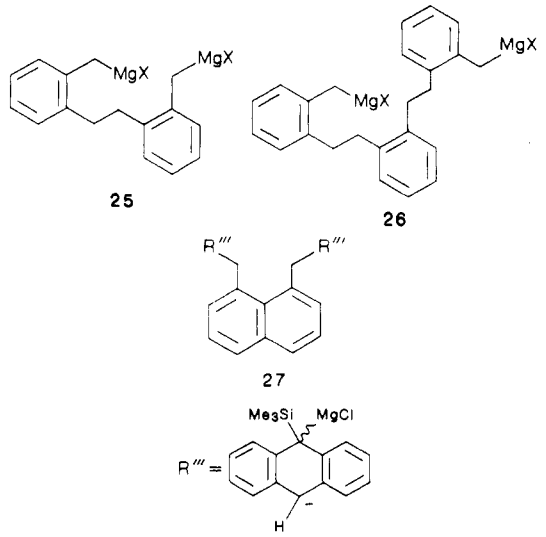


diminished on lowering the temperature. In the classical reaction the bromide results in formation of $(C_8H_8)_n$.[21] 1,4-Bis(chloromethyl)benzene with **1** at 20 °C gives a ca. 1:1 mixture of the di-Grignard reagent and the coupled di-Grignard reagent, isomeric with **25**. At −10 °C, however, formation of di-Grignard reagent **20b** in >90% yield results. There is no inherent problem with the 1,3-isomer as is the case for the classical method.[23]

Reagent **21** is accessible in high yield. The classical reaction yields a polymeric material derived from intermolecular coupling,[41] as does Rieke's magnesium. Solutions of reagents derived from **1** and **2** are stable for days whereas that derived from **5** reacts further, as is evident by a color change, pale brown to deep red. The offending reaction is nucleophilic substitution of the generated anthracene, eq 2, which is complete in ca. 90 h, yielding **27**. (Note: This product arises from a secondary reaction; the seemingly analogous products for many halides (see above) arise from addition as the primary process, Scheme I.) It is addition of an organomagnesium reagent to an aromatic ring. Such reactions usually require rather forcing conditions or electron-withdrawing substituents as in the present case.[42] Nevertheless, addition is slow enough not to be a serious problem in the use of magnesium–silyl–arene compounds in generating Grignard reagents. Di-Grignard reagent **21** is an implied intermediate in the Grignard in situ trapping reaction with $ClSiMe_3$.[41]

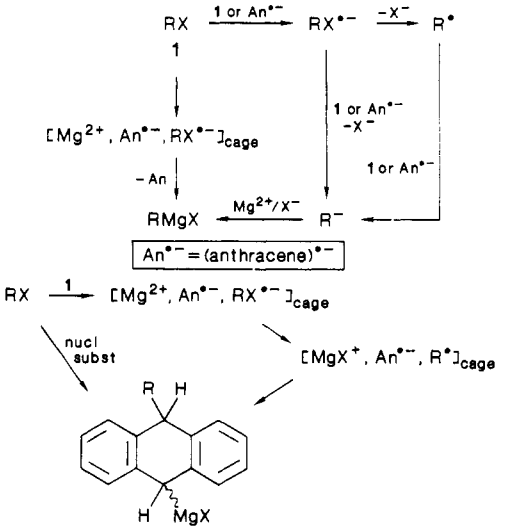
In the case of the formation of the axially dissymmetric di-Grignard reagents **22** and **23**, the competing reaction is exclusively intramolecular cyclization, the tendency for this being greater for the bromide than the chloride. While **22** is accessible in high yield by using the classical method, **23** is not. The latter is formed in ca. 43% yield from the corresponding dichloride under the critical conditions established for generating **22**.[24] The tri-Grignard reagent **24** is to our knowledge only the third to be prepared.[43]

Mechanism. Compounds **1–7** behave as if they undergo metal–carbon bond scission on delivering atomic magnesium to form Grignard reagents. The mechanism, however, involves electron-transfer reactions, which is the accepted mechanism in the classical reaction,[44] and also a mechanism in the reaction of organomagnesium reagents with organic halides.[25] This is based on the following: (i) the detection of radicals, most likely of anthracene, during Grignard reagent formation; (ii) magnesium–naphthalene radical anion compounds result in insertion of magnesium into C–O epoxide bonds via electron-transfer processes,[19] and that alkali-metal–arene compounds yield organometallic compounds via electron-transfer reactions;[29,30] (iii) formation of **16** involves conversion of the halide to $Ph_3C^{\bullet}$[36] prior to Grignard reagent formation, although this radical is exceptionally stable with respect to association in solution; (iv) formation of **10** using 2 molar equiv of **1** yields solutions containing the Grignard reagent and (anthracene)$^{\bullet-}$ (eq 4); (v) $[Mg(THF)_6]^{2+}[(\text{fluoranthene})^{\bullet-}]_2$, reported in part 1[5] gave the Wurtz-coupled product with benzyl chloride in THF, ca. 90% yield; (vi) $[Mg_2Cl_3(THF)_6]^+[\text{anthracene}]^{\bullet-}$, prepared by the method of Bogdanovic et al.,[10] was also effective in yielding Grignard reagents, at least with benzyl chloride and 1,2-bis(chloromethyl)benzene, eq 5. [Several experiments on both

$$2[Mg_2Cl_3(THF)_6]^+[\text{anthracene}]^{\bullet-} + RX \xrightarrow[-2C_{14}H_{10}]{-3MgCl_2(THF)_n} RMgX \quad (5)$$

halides and with different batches of the metal–arene compound gave a range of ratio of metal–arene to halide, 1.9–2.7, as judged by the discharge of the characteristic green color of (anthracene)$^{\bullet-}$; departure from 2.0 (theoretical) may be caused by difficulties in preparing pure metal–arene compound.] Thus, **1** and (anthracene)$^{\bullet-}$ can contribute to Grignard formation; **1** can yield the cage species [Mg^{2+}, (anthracene)$^{\bullet-}$, $RX^{\bullet-}$] which can collapse to RMgX whereas reactions involving (anthracene)$^{\bullet-}$ would yield initially $RX^{\bullet-}$ and/or $R^{\bullet}$. These then must encounter another (anthracene)$^{\bullet-}$ species to form RMgX. [Radical anion species present during Grignard formation may arise from the reaction of **1** with preformed anthracene and MgX_2 derived from a shift in the Schlenk equilibrium, $2RMgX \rightleftharpoons MgX_2 + MgR_2$.]

Scheme II



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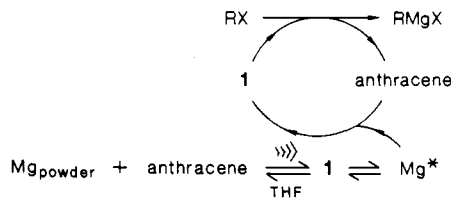
Scheme III



Scheme II depicts the likely sequence of electron-transfer reactions affording Grignard reagents and also addition products. For simplicity only compound 1 is considered, the reactions of the other metal–arene compounds 2–7 would be similar. The mechanism in Scheme II differs from that for the accepted mechanism for Grignard formation in that electron transfer is from anionic arene species (either in the bulk solution or as a cage with Mg^{2+} and $RX^{\bullet-}$) rather than some magnesium metal.[44] For metal–arenes the magnesium is already in the formal divalent state whereas with metal particles oxidation involving formally Mg(I) species,[44] and possibly Grignard magnesium clusters, RMg_nX,[45] occurs.

Given that compound 1 is formed from equilibration of magnesium with anthracene,[8] eq 6, it is unlikely that small

$$Mg^* + \text{anthracene} \rightleftharpoons 1 \qquad (6)$$

particles of magnesium are an active species in forming Grignard reagents since such particles would yield alkyl- and arylmagnesium halides, which are not detected. Moreover, Rieke's magnesium,[15] which is based on small particles, failed to give an appreciable amount of the di-Grignard reagent of 1,8-bis(chloromethyl)naphthalene at 0 and −78 °C.

Is it possible to form Grignard reagents via reaction of 1, and related compounds, formed in situ from activated magnesium and a catalytic amount of anthracene to try and overcome the objection of generating solutions of Grignard reagents loaded with anthracene? This was tested by reacting 1,8-bis(chloromethyl)naphthalene at −78° C with highly activated magnesium (Mg*) derived from extensive sonication of magnesium powder in THF with ca. 0.02 molar equiv of anthracene,[16c] Scheme III; extensive coupling was evident along with ca. 20% formation of the di-Grignard reagent **21**. This approach may have some merit for less difficult to prepare Grignard reagents. The main difficulties appear to be controlling the reaction of halide with 1 rather than at the active metal surface and the slow rate of formation of 1,[8] even at ca. 20 °C.

Greater coupling for organic bromides than chlorides for 8–24 is consistent with Br^- being a better leaving group than Cl^-, affording $R^\bullet$ from $RX^{\bullet-}$, Scheme II. It is also consistent with bond energy differences; C – Cl is greater than C – Br. That is, loss of Br^- is more favored both kinetically and thermodynamically.

In the absence of radical intermediates (ESR) where addition occurs, Scheme I, two pathways are plausible, namely, concerted nucleophilic substitution and formation of the diradical cage [Mg^{2+}, (anthracene)$^{\bullet-}$, $RX^{\bullet-}$], Scheme II. If the latter prevails, the cage must collapse instead of releasing $RX^{\bullet-}$ and/or $R^\bullet$. This is conceivable considering the lower stability of such radicals relative to those based on allylic, benzylic, and tris(trimethylsilyl)methyl moieties. In addition, the absence of Grignard or coupled product rules out formation of $RX^{\bullet-}$ and/or $R^\bullet$.

Where nucleophilic substitution prevails, the addition of transition-metal halides can make electron-transfer reactions more favorable.[25b,46] Thus if nucleophilic substitution is the mechanism in the present study, such metal halides might favor formation of Grignard reagents. However, in several reactions of alkyl halides with 1 in the presence of ca. 0.02 molar equiv of $FeCl_3$ which rapidly reacts with 1 yielding brown solutions, no Grignard reagent or coupled product was evident.

Experimental Section

General. Techniques and procedures for drying solvents are described in part 1.[5] Benzyl halides, allyl halides, crotyl bromide, benzhydryl chloride, trityl halides, and the 1,*n*-bis(halogenomethyl)benzenes, *n* = 2, 3, and 4, were purchased from Fluka and 9-(chloromethyl)anthracene was purchased from Alfa. Compounds 1–7,[5-9] 4-*tert*-butyl-2,6-dimethyl-1-(chloromethyl)benzene,[47] 2-(chloromethyl)pyridine,[48] 8-(bromomethyl)quinoline,[49] 1-halogeno-1-phenylethanes,[50] 1-(halogenophenyl)propanes,[51] (bromophenylmethyl)trimethylsilane,[40a] 1,8-bis(chloromethyl)-naphthalene,[41] 2,2′-bis(halogenomethyl)biphenyl,[24] 2,2′-bis(bromomethyl)-1,1′-binaphthyl,[52] and 1,3,5-tris(bromomethyl)-benzene[53] were prepared using literature procedures. 2,2′-Bis-(chloromethyl)-1,1′-binaphthyl and 1,3,5-tris(chloromethyl)-benzene were prepared by treating the corresponding bromides with excess LiCl in DMF (*N*,*N*′-dimethylformamide) as detailed below for the synthesis of 8-(chloromethyl)quinoline. 9-(Bromomethyl)anthracene was similarly prepared from the chloride by using excess LiBr.

Synthesis of 8-(Chloromethyl)quinoline. 8-(Bromomethyl)quinoline (5.0 g, 22.6 mmol) was dissolved in DMF (100 mL) and excess LiCl (4.8 g, 113 mmol) was added. After 2 h, water (200 mL) and hexane (300 mL) were added, the hexane layer was separated, and solvent was removed in vacuo, yielding a white powder. Recrystallization from hexane gave white needles of the title compound: yield 3.2 g, 75%; mp 56 °C (lit.[54] mp 56 °C).

Synthesis of *meso*- and *rac*-1,2-Bis[bromo(trimethylsilyl)methyl]benzene. A stirred mixture of 1,2-bis[(trimethylsilyl)methyl]benzene (10.0 g, 40 mmol), *N*-bromosuccinimide (14.6 g, 82 mmol), and CCl_4 (100 mL) was refluxed for 1 h while being irradiated with a 200-W lamp. Upon cooling to ca. 20 °C, the mixture was filtered and the filtrate concentrated in vacuo. The residue was taken up in hexane (100 mL), washed with water, dried over anhydrous $MgSO_4$, and then concentrated in vacuo. The product was distilled as a colorless oil (112–114 °C/10^{-2} mmHg) which solidified over 2 weeks at −30 °C (mp 38–40 °C). Anal. Found: C, 41.45; H, 5.85; Br, 38.15. Calcd for $C_{14}H_{24}Br_2Si_2$: C, 41.18; H, 5.92; Br, 39.14. ^1H NMR (300 MHz, chloroform-*d*): δ 0.17 (s, 18 H, Si*Me*), 0.22 (s, 18 H, Si*Me*), 4.55, 4.59 (s, 2 H, C*H*Si), 7.14, 7.36 (m, C_6H_4). ^{13}C NMR (75.4 MHz, chloroform-*d*, ^1H decoupled): δ −2.4, −1.7 (SiMe), 38.9 (*C*HSi), 127.1, 127.6, 130.1, 130.5 ($C_2(CH)_4$), 137.3, 138.7 ($C_2(CH)_4$).

Reaction of 1–7 with Organic Halides. Only one reaction in THF is given here, viz. synthesis of **21** using **5** as the source of magnesium. Specific details on yield, reaction temperature, and other features are in Table I.

To a stirred slurry of **5** (3.7 g, 7.6 mmol) in THF (50 mL), held at 0 °C, was slowly added over 30 min a THF solution of 1,8-bis(chloromethyl)naphthalene (0.85 g, 3.8 mmol). After addition of ca. 2 mL of the halide solution the reaction mixture attained a deep green color which persisted until addition of the last few

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drops whereupon it turned deep brown. Aliquots (2 mL) were quenched with 0.1 mol dm^{-3} aqueous HCl and then back titrated with 0.1 mol dm^{-3} aqueous NaOH, activity ca. 95%. A 25-mL aliquot was treated with $ClSiMe_3$ and after 12 h the THF was removed in vacuo. GC/MS analysis of a hexane extract showed that 1,8-bis[(trimethylsilyl)methyl]naphthalene was the exclusive product. The remainder of the original reaction mixture was left for 3 days during which a deep red/brown precipitate formed. This was collected and washed with THF (2 × 10 mL), and 0.1 mol dm^{-3} aqueous HCl was then added to a slurry of this material in THF (10 mL) yielding a white precipitate. This was collected and recrystallized from diethyl ether as fine white needles as one of the isomers of the conjugate acid of compound **27** possessing C_2 symmetry, 1.1 g, 43% yield, mp 230–231 °C. Anal. Found: C, 83.85; H, 7.45. Calcd for $C_{46}H_{48}Si_2$: C, 84.09; H, 7.36. ^1H NMR (80 MHz, chloroform-*d*): δ 0.30 (s, 18 H, Si*Me*), 3.95 (m, 8 H, C*H*Si, C*HCH*$_2$), 6.2–7.9 (m, 22 H, C*H*$_{aromatic}$); ^{13}C NMR (20.1 MHz, chloroform-*d*, ^1H decoupled): δ 0.2 (Si*Me*), 40.2 (*C*HCH$_2$), 47.3 (*C*HSi) 47.9 (*C*H$_2$), 124.3, 125.8, 127.3, 129.1, 129.4, 132.4 (*C*H$_{aromatic}$), 131.2, 135.2, 135.7, 136.2, 138.4 (*C*$_{aromatic}$). MS: *m/e* 657 (M^+).

Data of new silicon compounds derived from quenching Grignard reagents **9** and **17** with $ClSiMe_3$ (and prepared by the in situ trapping of the Grignard reagents generated by using magnesium metal in THF in ca. 80% yield) are as follows. 4-*tert*-Butyl-2,6-dimethyl-1-[(trimethylsilyl)methyl]benzene, distilled as a colorless liquid, 135–136 °C, at 10^{-2} mmHg. Anal. Found: C, 77.50; H, 11.10. Calcd for $C_{16}H_{28}Si$: C, 77.34; H, 11.36. ^1H NMR (80 MHz, chloroform-*d*): δ 0.21 (s, 9 H, Si*Me*), 1.47 (s, 9 H, C*Me*$_3$), 2.29 (s, 2 H, C*H*$_2$), 2.40 (s, 6 H, C*Me*) 7.16 (s, 2 H, C$_6$*H*$_2$). ^{13}C NMR (20.1 MHz, chloroform-*d*, ^1H decoupled): δ −0.2 (si*Me*), 19.6 (*CH*$_2$), 21.3 (C*Me*), 31.4 (C*Me*$_3$), 124.8 ((*CH*)$_2$C$_4$), 134.1, 134.8, 146.2 ((CH)$_2$*C*$_4$). MS: *m/e* 248 (M^+). 1-(Trimethylsilyl)-1-phenylpropane, distilled as a colorless liquid, 47–48 °C, at 5 mmHg. Anal. Found: C, 74.75; H, 10.35. Calcd for $C_{12}H_{20}Si$: C, 74.95, H, 10.47. ^1H NMR (300 MHz, chloroform-*d*): δ 0.17 (s, 9 H, Si*Me*), 0.95 (t, 3 H, *J* = 7.1 Hz, C*Me*), 1.90 (m, 3 H, *CH*$_2$,*CH*), 7.20 (m, 5 H, C$_6$*H*$_5$). ^{13}C NMR (75.4 MHz, chloroform-*d*, ^1H decoupled) δ 2.9 (Si*Me*), 14.3 (C*Me*), 22.5 (*CH*$_2$), 39.3 (CH), 124.2, 127.7, 128.0 ((CH)$_5$C) 143.7 ((CH)$_5$*C*). MS: *m/e* 192 (M^+).

Reaction of 4 with (±)-1-Chloro-1-phenylethane in Toluene. To a stirred slurry of **4** (1.3 g, 3 mmol) in toluene (15 mL) was added 1-chloro-1-phenylethane (0.43 g, 3 mmol) in toluene (15 mL). A yellow precipitate remained after 12 h and an acid-quenched aliquot indicated 85% formation of the Grignard reagent. The mixture was then transferred by cannula into a toluene/dry ice slurry and after 12 h the solvent was removed in vacuo and 2 mol dm^{-1} of NaOH added. The mixture was washed with hexane and then acidified and extracted with diethyl ether. Concentration and distillation in vacuo gave 2-phenylpropionic acid. Yield 0.3 g, 70%; $[\alpha]_D$ +6.6° (EtOH); cf. +81° for resolved material.[55]

Acknowledgement is made to the Australian Research Grants Scheme for support of this research, to C. Eaborn for a sample of tris(trimethylsilyl)methyl chloride, and to M. V. Sargent for many helpful discussions.

Registry No. **1**, 86901-19-1; **2**, 114679-04-8; **3**, 109889-35-2; **4**, 109906-74-3; **5**, 100908-25-6; **6**, 114679-05-9; **7**, 100908-24-5; **9**, 114693-85-5; **10** (X = Cl), 96693-22-0; **10** (X = Br), 114693-86-6; **13**, 114693-87-7; **14** (X = Cl), 114693-88-8; **14** (X = Br), 114693-89-9; **15** (X = Cl), 114693-90-2; **16** (X = Cl), 34324-92-0; **17a** (X = Br), 41745-02-2; **17b** (X = Cl), 114693-91-3; **17b** (X = Br), 114693-92-4; **18**, 57482-85-6; **19a** (X = Cl), 78499-87-3; **19a** (X = Br), 114693-93-5; **19b** (X = Br, isomer 1), 114693-94-6; **19b** (X = Br, isomer 2), 114693-95-7; **20a** (X = Cl), 114693-96-8; **20a** (X = Br), 114693-97-9; **20b** (X = Cl), 114693-98-0; **21**, 96693-26-4; **22** (X = Cl), 84609-48-3; **22** (X = Br), 96693-23-1; **23** (X = Cl), 96693-24-2; **23** (X = Br), 96693-25-3; **24** (X = Cl), 114693-99-1; **24** (X = Br), 114694-00-7; **25** (X = Cl), 114694-01-8; **26** (X = Cl), 114694-02-9; **27** (conjugate acid), 114694-03-0; *o*-TMSCH(Br)C$_6$H$_4$CH(Br)TMS (isomer 1), 114694-04-1; *o*-TMSCH(Br)C$_6$H$_4$CH(Br)TMS (isomer 2), 114694-05-2; PhCH(Me)CH(Me)Ph, 5789-35-5; PhCH(Et)CH(Et)Ph, 5789-31-1; *p*-ClMgCH$_2$C$_6$H$_4$(CH$_2$)$_2$C$_6$H$_4$CH$_2$MgCl-*p*, 114694-06-3; (Me$_3$Si)$_3$CMgCl, 114694-07-4; 2,6-dimethyl-4-*tert*-butylbenzyl chloride, 19387-83-8; 9-anthrylmethyl chloride, 24463-19-2; 8-(chloromethyl)quinoline, 94127-04-5; phenyl(trimethylsilyl)methyl bromide, 17903-41-2; bis(2-chloromethyl)-1,1′-binaphthalene, 96693-27-5; 9-anthrylmethyl bromide, 2417-77-8; bis(2-bromomethyl)-1,1′-binaphthalene, 54130-90-4; 1,2-bis[(trimethylsilyl)methyl]benzene, 18412-14-1; 9-[(trimethylsilyl)methyl]anthracene, 88920-42-7; 8-[(trimethylsilyl)methyl]quinoline, 105212-20-2; 1,8-bis[(trimethylsilyl)methyl]naphthalene, 57754-03-7; 4-*tert*-butyl-2,6-dimethyl-1-[(trimethylsilyl)methyl]benzene, 114694-08-5; (±)-1-chloro-1-phenylethane, 38661-82-4; 1-(trimethylsilyl)-1-phenylpropane, 18027-67-3.

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Nickel(0)-Catalyzed Cycloaddition of Diynes and Carbon Dioxide to Bicyclic α-Pyrones

Tetsuo Tsuda,* Shohei Morikawa, Ritsuo Sumiya, and Takeo Saegusa*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan 606

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$Ni(COD)_2$–trialkylphosphine catalysts effected the cycloaddition of CO_2 and terminally dialkyl-substituted diynes RC≡CCH$_2$–Z–CH$_2$C≡CR (**1**) (**1a**, Z = CH$_2$, R = Et; **1b**, Z = CH$_2$CH$_2$, R = Et; **1c**, Z = CH$_2$CH$_2$CH$_2$, R = Et; **1d**, Z = CH$_2$CH$_2$, R = Me; **1e**, Z = CH$_2$CH$_2$, R = *n*-Bu; **1f**, Z = CH$_2$CH$_2$, R = *sec*-Bu; **1g**, Z = O, R = Et; **1h**, Z = N-*n*-Pr, R = Et) to afford 3,6-dialkyl-4,5-cycloalkano-α-pyrones (**2**) in one step. Trialkylphosphines such as tri-*n*-alkyl- and tri-*sec*-alkylphosphines were the effective ligands. The structure of **1** had an influence upon the formation of **2**: each diyne **1** required its own suitable trialkylphosphine ligand. By the proper use of the phosphine ligand, the bicyclic α-pyrones **2** were obtained in 50–90% yields from diynes **1a–h** except **1c**. The diyne dimerization product **3** was formed as a byproduct in the formation reaction of **2d** from **1d**. This finding suggests that the bicyclic α-pyrone formation competes with the diyne oligomerization. Under the condition where the diynes **1a** and **1b** produced bicyclic α-pyrones **2a** and **2b** efficiently, the cycloaddition of the monoyne, e.g., 4-octyne, with CO_2 failed.

Utilization of carbon dioxide in a transition metal catalyzed synthesis of complex organic molecules is an interesting problem and has received considerable attention in recent years.[1] Transition metal catalyzed CO_2 fixation

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