any of the "MOM-OH" dimer **8**. Therefore, **8** does not arise by partial hydrolysis of **9**. Indeed, we were unable to prepare the "diMOM" dimer **9** by radical coupling of **7** using AIBN/Bu$_3$SnH, but instead had to resort to flash vacuum pyrolysis.[17] Traces of oxygen or Cu(II) salts are known to initiate dimerization of organocuprates.[1] Homochiral cuprate **2** was prepared in THF, and Cu(II) salts and oxygen were added in separate experiments. Upon aqueous quench, the Cu(II) addition reaction provided only protonated material while the oxygen addition reaction did provide **8** in 40% yield. GC analysis of **8** from the oxygen dimerization reaction determined that the % de corresponded to that obtained by simple condensation of the α-alkoxyorganolithio anion with hexanal. Mosher esterification and ^{19}F NMR analysis of **8** revealed that the dimer had been obtained with >90% retention of configuration! This unexpected result implies that racemization of the α-alkoxyalkyl ligand does not occur during cuprate formation (Li to Cu transmetalation), but most likely occurs during the 1,4-addition reaction. Equilibration of the cuprate and free RLi species is not a reasonable explanation for dimer formation given the fact that 1,2-addition to the enone is not observed.[18] In addition, the cuprate **2** does not add to aliphatic aldehydes even in the presence of trimethylsilyl chloride. The dimer **8** may arise by an oxygen-catalyzed decomposition pathway which produces hexanal and RLi. Rapid 1,2-addition of the lithio species to the aldehyde (perhaps mediated by a Cu template?) would then occur providing optically active **8**. Single electron transfer processes were initially proposed as the mechanism of cuprate 1,4-addition.[2c] Previous studies have indicated that electron-transfer processes from cuprates are restricted in polar solvents such as THF and by the use of additives such as trimethylsilyl chloride.[2h] The reaction conditions employed in this study were therefore not optimal for electron transfer. Arguments favoring a stepwise process of d-π^* complexation followed by a reversible β-Cu(III) intermediate have also been offered.[2d–i] Racemization of the transferable ligand observed in the 1,4-addition reactions of **2** during a direct oxidative addition of the cuprate to the enone or in a final reductive elimination step seems unlikely. Apparently, adventitious oxygen leads to the initiation of the racemization process (mechanism unknown) as well as dimerization. 1,4-Addition occurs at a faster relative rate than dimerization; however, racemization is extremely facile only for the 1,4-addition reaction. Even the small amounts of "MOM-OH" dimer **8** isolated from the 1,4-addition reactions to cyclohexenone exhibit a significant level of optical activity ($\geq$80% retention of configuration).

Early work in cuprate chemistry revealed that cuprate reagents could undergo 1,4-addition reactions with retention of configuration (relative), and other more recent examples have also been reported.[19] The results presented in this paper indicate that more than one mechanism may be operative for organocuprate 1,4-addition.[2] The reaction pathway may be dependent on the type of cuprate[2h] and the transferable ligand as well as the substrate.[20] Secondary homochiral α-alkoxyorganocuprates can undergo 1,4-addition reactions with complete retention of configuration; however, this result is not readily reproducible. Further studies on the racemization of these organocuprate reagents and the novel formation of optically active dimeric species by oxidative dimerization processes are underway.

Acknowledgment. R.J.L. would like to thank the American Cyanamid Co. for an Academic Award (1989) and B.D.G. thanks the Burroughs-Wellcome Fund for fellowship support.

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[17] Selenide **7** was subjected to flash vacuum pyrolysis conditions reported for alkyl, aryl selenides (650 °C, 0.5 mmHg); Misumi, S.; Higuchi, H.; Otsubo, T.; Ogura, F.; Yamaguchi, H.; Sakata, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 182–187.

[18] Lipshutz and co-workers have provided NMR evidence for equilibration processes in Gilman reagents: Lipshutz, B. H.; Kozlowski, J. A.; Breneman, C. M. *J. Am. Chem. Soc.* **1985**, *107*, 3197–3204. Higher order (HO) cyano cuprates apparently do not exhibit the same characteristics in that free RLi is not present. For recent discussions on the solution structures of HO cyano cuprates, see: Lipshutz, B. H.; Sharma, S.; Ellsworth, E. L. *J. Am. Chem. Soc.* **1990**, *112*, 4052–4054. Bertz, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 4051–4052.

[19] See, inter alia: (a) Whitesides, G. M.; Kendall, P. E. *J. Org. Chem.* **1972**, *37*, 3718–3725. (b) Morgans, D. J.; Feigelson, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 5477–5479.

[20] For more recent mechanistic discussion, see: (a) Dorigo, A. E.; Morokuma, K. *J. Am. Chem. Soc.* **1989**, *111*, 6524–6536. (b) Corey, E. J.; Hannon, F. J. *Tetrahedron Lett.* **1990**, *31*, 1393–1396. Evidence for multiple reaction pathways has been presented by several research groups, see ref 2 and references cited therein.

Palladium-Catalyzed Reductive Coupling of Aromatic Acid Chlorides with Disilanes

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Summary: Electron-deficient aromatic acid chlorides are converted to biphenyl compounds by palladium-catalyzed reaction with disilanes.

Synthetic routes to biphenyl derivatives remain limited.[1] Ullmann coupling of aryl halides with copper or nickel and Gomberg–Bachman coupling of arenes with aromatic diazonium salts are often employed, but both methods have drawbacks. Other traditional approaches involve stoichiometric use of organometallic reagents, such as Grignards, arylthallium, arylmercury, and aryllithium compounds, or require forcing conditions as with Friedel–Crafts arylation. Limitations inherent in these and other routes have fostered continuing interest in a variety of new synthetic methods including modified Ullmann reactions, coupling of tellurium and bismuth reagents, aryltin reactions, cross-coupling reactions, and others.[2] In this context

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[1] For overviews of this area, see: (a) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985. (b) Sainsbury, M. *Tetrahedron* **1980**, *36*, 3327.

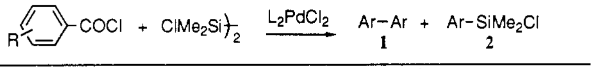
Table I. Effect of Reaction Conditions and Catalyst on Selectivity[a]

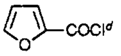
$$\mathrm{ArCOCl} + \mathrm{ClMe_2Si}\big)_2 \xrightarrow{\mathrm{L_2PdCl_2}} \underset{\mathbf{1}}{\mathrm{Ar{-}Ar}} + \underset{\mathbf{2}}{\mathrm{Ar{-}SiMe_2Cl}}$$

no.	solvent	*T*, °C	L	% convn	% **1**[b]	% **2**[c]
1	neat	150	PPh_3	100	10	82
2	neat	165	PPh_3	100	26	66
3	neat	195	PPh_3	100	33	40
4	nitrobenzene	165	PPh_3	100	25	59
5	mesitylene	165	PPh_3	100	72	21
6	nitrobenzene	125	PPh_3	100	0	90
7[d]	mesitylene	165	PPh_3	100	76	20
8	mesitylene	165	$P(Ph\text{-}p\text{-}Me)_3$	100	42	43
9	mesitylene	165	$P(Ph\text{-}p\text{-}F)_3$	83	64	15
10	mesitylene	165	pyridine	70	16	50
11	mesitylene	165	$Ph_2PCH_2PPh_2$	100	85	9
12	mesitylene	165	$Ph_2P(CH_2)_2PPh_2$	95	76	17
13	mesitylene	165	$Ph_2P(CH_2)_3PPh_2$	100	57	33
14	mesitylene	165	$(C_6F_5)_2P(CH_2)_2P(C_6F_5)_2$	38	1	34

[a] Ar = 3,4-dicarboxylic acid anhydride. Catalyst loading was 1000 ppm Pd. Percent conversion was determined by GC. Bond formation was to the ipso carbon for **1** and **2** as determined by ^{1}H NMR. [b] Isolated yield. [c] Yield based on NMR integration versus internal standard. [d] Hexamethyldisilane.

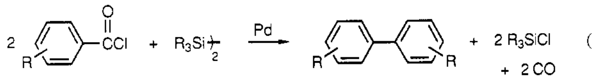
Table II. Substituent Effects on Reaction Selectivity[a]



R	% **1**[b]	% **2**[c]
3,4-dicarboxylic acid anhydride	72	21
3,4-dicarboxylic *N*-methylimide	24	44
p-COCl	22	52
m-NO_2	30	50
H	0	83
acid chloride = 	80	0

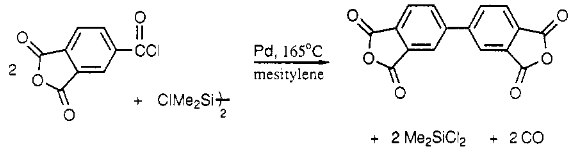
[a] Reactions were run to 100% conversion (determined by GC) in mesitylene at 165 °C with $(Ph_3P)_2PdCl_2$ (1000 ppm Pd). [b] Isolated yields. Compounds were identified by mass spectra and/or ^{1}H NMR. [c] Yield based on NMR integration vs internal standard. [d] Neat reaction run at 145 °C.

we report a new carbon–carbon coupling process in which electron-deficient aromatic acid chlorides undergo reaction with disilanes to give biphenyl compounds (eq 1).[3] The palladium-catalyzed reaction involves reductive coupling of the acid chloride with concomitant decarbonylation. Disilane functions as a stoichiometric reductant. Arene coupling by other methods is usually accompanied by salt generation which is avoided here through formation of chloromonosilanes.



(1)

Trimellitic anhydride acid chloride and dichlorotetramethyldisilane undergo reaction in refluxing mesitylene to form biphenyl dianhydride, BIDA, in 85% yield (eq 2).[4]



(2)

Under these conditions, dimethyldichlorosilane (bp 68 °C) is removed continuously. The product precipitates from solution and is isolated in purity suitable for polymer synthesis. This is a potentially important application of the new method since BIDA is a commercial product which is increasingly used in high-temperature polymers and other materials.[7] The industrial route to BIDA involves oxidative coupling of dimethyl phthalate under high oxygen pressure.[8] The process yields a mixture of regioi-

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(2) For some recent examples, see: (a) Barton, D. H. R.; Ozbalik, N.; Ramesh, M. *Tetrahedron* **1988**, *44*, 5661. (b) Barton, D. H. R.; Ozbalik, N.; Ramesh, M. *Tetrahedron Lett.* **1988**, *29*, 3533. (c) Lourak, M.; Vanderesse, R.; Fort, Y.; Caubere, P. *Tetrahedron Lett.* **1988**, *29*, 545. (d) Amatore, C.; Jutand, A. *Organometallics* **1988**, *7*, 2203. (e) Takahashi, H.; Ohe, K.; Uemura, S.; Nobuyuki, S. *J. Organomet. Chem.* **1988**, *350*, 227. (f) Cheng, J.; Luo, F. *Tetrahedron Lett.* **1988**, *29*, 1293. (g) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. (h) Ghosal, S.; Luke, G. P.; Kyler, K. S. *J. Org. Chem.* **1987**, *52*, 4296. (i) Stossel, D; Chan, T. H. *J. Org. Chem.* **1987**, *52*, 2105. (j) Mitsubishi Chemical Industries Co., Ltd. Japanese Patent JP 62 72,629 [87 72,629]. (k) Sharp, M. J.; Cheng, W.; Snieckus, V. *Tetrahedron Lett.* **1987**, *28*, 5093. (l) Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627.

(3) (a) Presented in part at the XXI Organosilicon Symposium, June 3–4, 1988, Montreal. (b) Krafft, T. E.; Rich, J. D.; McDermott, P. J.; Chang, T. C. U.S. Patent Appl. 187,783 (1988) to General Electric Co.

(4) In a typical reaction trimellitic anhydride acid chloride (10.53, g, 0.05 mol), $Pd(PhCN)_2Cl_2$[5] (19.2 mg, 0.05 mmol), $Ph_2PCH_2PPh_2$ (19.2 mg, 0.05 mmol), and anhydrous mesitylene (10 mL) were placed in a 50-mL round-bottom flask fitted with a claisen tube and still head. The mixture was heated to reflux under a nitrogen atmosphere, and dichlorotetramethyldisilane[6] (9.36 g) was then added over a 4-h period. Visible gas evolution was noted immediately upon addition of disilane, and dimethyldichlorosilane began distilling from the reaction mixture. The reaction was stopped after a total of 18 h and cooled to room temperature. Residual chloromonosilane and unreacted disilane were removed under vacuum, and the mixture was stirred with CCl_4 (5 mL) to insure complete precipitation of the product. The product was isolated by filtration and washed with CCl_4: yield was 6.24 g (85%). The filtrate was stripped of solvent and analyzed for arylsilane by ^{1}H NMR integration vs a known quantity *p*-dimethoxybenzene. The identity of the biphenyl product was confirmed by mass spectroscopy and by comparison of its ^{1}H NMR spectrum with that of an authentic sample. ^{1}H NMR DMSO-d_6): δ 8.62 (s, 2 H), 8.49 (d, 2 H, J = 8.5 Hz), 8.22 (d, 2 H, J = 8.5 Hz). High-resolution electron impact mass spectrum: calcd for $C_{16}H_6O_6$ 294.0164 amu, experimental 294.0164 amu.

(5) Kharasch, M. L.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

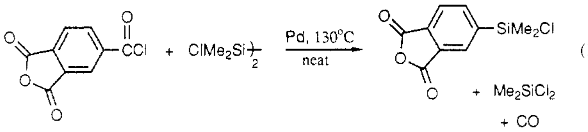
(6) A modified literature procedure was used to obtain tetrachlorodimethyldisilane by photochemical coupling of chlorodimethylsilane. See: (a) Nay, M.; Woodall, G.; Strausz, O.; Gunning, H. *J. Am. Chem. Soc.* **1965**, *87*, 179. (b) Reedy, D.; Urry, G. *Inorg. Chem.* **1967**, *6*, 2117.

(7) For example, see: (a) General Electric Co. U.S. Patent 4,634,760 (1987). (b) Ube Industries, Ltd., U.S. Patent 4,568,715 (1986). (c) Nitto Electrical Industries U.S. Patent 4,499,042 (1985). (d) Ube Industries, Ltd., U.S. Patent 4.290.936 (1981). (e) Ube Industries, Ltd., U.S. Patent 4.247,443 (1981).

(8) (a) Ube Industries, Ltd., U.S. Patent 4,581,469 (1986). (b) Ube Industries, Ltd., U.S. Patent 4,338,456 (1982). (c) Ube Industries, Ltd., U.S. Patent 4,292,453 (1981). (d) Itatani, H.; Yoshimoto, H. *J. Org. Chem.* **1973**, *38*, 76.

somers which requires separation and conversion to the anhydride. Synthesis according to eq 2 offers an attractive alternative which avoids high pressure and selectively yields the desired 3,4,3′,4′ isomer from readily available starting materials.[9]

Important features of the new process include large solvent and temperature effects. High temperature and nonpolar solvents favor the carbon–carbon coupling reaction shown in eq 2. At lower temperature and in polar environments (neat or in nitrobenzene) the same reactants undergo silylative decarbonylation to yield aromatic silane (eq 3).[10,11] Changes in solvent and temperature act synergistically and together have a dramatic effect on selectivity (Table I, entries 1–6). Palladium(II) phosphine complexes, L_2PdCl_2, were employed as catalysts, and significant differences in selectivity were obtained by changing ligands (Table I, entries 5 and 8–14).



(3)

Formation of biphenyl derivatives has been demonstrated with other electron-withdrawing substituents on the ring. Terephthalloyl chloride, *m*-nitrobenzoyl chloride, or trimellitic anhydride acid chloride *N*-methylimide gave mixtures of biaryl and arylsilane (Table II). Yields of biaryl for these substrates have not yet been optimized. In each case the biphenyl product was derived from regioselective coupling at the ipso carbons. In the absence of electron-withdrawing substituents (e.g. benzoyl chloride), no biphenyl was formed. Surprisingly, under conditions which normally favor silylation (neat, 145 °C), 2-furanoyl chloride yielded bifuran in high yield.

Other features of the reaction include efficient extrusion of CO at temperatures well below those normally required in palladium-catalyzed decarbonylations.[12,13] Earlier work suggests that the presence of disilane facilitates CO extrusion[10a] and that the efficiency of the decarbonylation step is highly dependent on the presence of at least one chloride on the disilane.[10c] Under conditions which favor carbon–carbon coupling, this disilane substituent effect is not operative, and decarbonylation proceeds equally with chloromethyldisilanes or hexamethyldisilane (Table I, entry 7). The coupling chemistry observed here for acid chlorides has not been reported for palladium-catalyzed reactions of aryl halides with disilane, even when run under similar conditions.[14] This suggests different Pd–Ar intermediates for the two reactions. Attempts to extend the methodology to reductants other than disilane have been unsuccessful. For example, substitution of disilane with dihydrogen or triethylsilane gives the known conversion to aldehyde.[15,16]

Stille has reported biaryl synthesis by palladium-catalyzed reaction of aryltriflates with distannanes.[2g] The process involves formation of an aryltin intermediate which subsequently couples with aryltriflate to yield the final product.[17] The analogy here would be initial formation of arylsilane (eq 4) followed by coupling with acid chloride. Reaction of trimellitic anhydride acid chloride and 4-(chlorodimethylsilyl)phthalic anhydride under normal coupling conditions yielded no detectable coupling (eq 5), even after a small amount of disilane was added to insure the presence of active catalyst.[18] This result, which is consistent with lower reactivity for silicon–carbon bonds than tin–carbon bonds,[19] suggests that arylsilane is not an intermediate in biphenyl formation.

$$\mathrm{Ar{-}COCl} + \left.\mathrm{ClMe_2Si}\!-\!\right)_2 \xrightarrow{\mathrm{Pd}} \mathrm{Ar{-}SiMe_2Cl} \qquad (4)$$

$$\mathrm{Ar{-}COCl} + \mathrm{Ar{-}SiMe_2Cl} \xrightarrow[\text{mesitylene}]{\mathrm{Pd},\ 165\,^{\circ}\mathrm{C}}\!\!\!\!\!\!\!\!\times\quad \mathrm{Ar{-}Ar} \qquad (5)$$

The results presented here constitute a new method for aromatic carbon–carbon bond formation from readily available starting materials which avoids salt formation and stoichiometric consumption of metal reductants. The synthetic utility of the reaction has been demonstrated in the case of biphenyldianhydride. The dramatic selectivity differences illustrated in Table I suggest that the scope of the reaction could be significantly broadened. Future work will address both the scope and mechanism of the reaction.

Acknowledgment. We thank Drs. Tony Chang, Jeffrey Wengrovius, and Kenneth Smith for helpful discussions and Mr. Steve Dorn for mass spectral data.

Supplementary Material Available: Experimental data for reactions summarized in Tables I and II (4 pages). Ordering information is given on any current masthead page.

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[9] Chloromethyldisilanes are formed in large quantity during industrial production of methylchlorosilanes. See: (a) Ward, W. J.; Ritzer, A.; Carroll, K. M.; Flock, J. W. *J. Catal.* **1986**, *100*, 240. (b) Voorhoeve, R. J. H. *Organohalosilanes: Precursors to Silicones*; Elsevier: Amsterdam, 1967.

[10] (a) Rich, J. D *J. Am. Chem. Soc.* **1989**, *111*, 5886. (b) Rich, J. D. *Organometallics* **1989**, *8*, 2606. (c) Rich, J. D.; Krafft, T. E. *Organometallics* **1990**, *9*, 2040.

[11] (a) Rich, J. D. U.S. Patent 4,709,054 (1987) to General Electric Co. (b) Rich, J. D. U.S. Patent 4,604,477 (1986) to General Electric Co.

[12] (a) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985. (b) Verbicky, J. W.; Dellacoletta, B. A.; Williams, L. *Tetrahedron Lett.* **1982**, *23*, 371. (c) Tsuji, J. *Organic Synthesis Via Metal Carbonyls, Vol. II*; Wiley: New York, 1977. (d) Ohno, K.; Tsuji, J. *J. Am. Chem. Soc.* **1968**, *90*, 99.

[13] Spencer has also reported palladium-catalyzed decarbonylation at temperatures below those normally required. See: Blaser, H.; Spencer, A. *J. Organomet. Chem.* **1982**, *233*, 267.

[14] (a) Eaborn, .; Griffiths, R. W.; Pidcock, A. *J. Organomet. Chem.* **1982**, *225*, 331. (b) Matsumoto, H.; Shono, K.; Nagai, Y. *J. Organomet. Chem.* **1981**, *208*, 145. (c) Matsumoto, H.; Yoshihiro, K.; Nagashima, S.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1977**, *128*, 409. (d) Matsumoto, H.; Nagashima, S.; Yoshihiro, K.; Nagai, Y. *J. Organomet. Chem.* **1975**, *85*, C1.

[15] House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin Cummings: Menlo Park, CA, 1972.

[16] (a) Corriu, R. J. P.; Lanneau, G. F.; Perrot, M. *Tetrahedron Lett.* **1988**, *29*, 1271. (b) Dent, S. P.; Eaborn, C.; Pidcock, A. *J. Chem. Soc., Chem. Commun.* **1970**, 1703. (c) Citron, J. D. *J. Org. Chem.* **1969**, *34*, 1977.

[17] The same mechanism is probably operative in palladium-catalyzed reactions of aromatic acid chlorides with distannanes which gives some coupling products. See: Bumagin, N. A.; Gulevich, Y. V.; Beletskaya, I. P. *J. Organomet. Chem.* **1985**, *282*, 421.

[18] Trimellitic anhydride acid chloride (10.54 g, 0.05 mol) and 4-(chlorodimethylsilyl)phthalic anhydride (12.04 g, 0.05 mol) were heated together with $Pd(PhCN)_2Cl_2$ (38.4 mg, 0.1 mmol) and Ph_3P (52.4 mg, 0.2 mmol) in mesitylene (20 mL) at 165 °C. During 1 h of heating no gas evolution was observed. NMR integration showed no change in the intensity of the Si–Me signal. A small quantity of disilane (0.187 g, 1.0 mmol) was then added, and the mixture heated for 19 h at 165 °C. NMR again indicated that no reaction had taken place.

[19] For example, see: (a) Cotton, F. A.; Wilkinson, G. *Advance Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 265–304. (b) Armitage, D. A. In *Comprehensive Organometallic Chemistry, Vol. 2*; Wilkinson, G., Stone, F. G., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; pp 1–203. (c) Davies, A. G. In *Comprehensive Organometallic Chemistry, Vol. 2*; Wilkinson, G., Stone, F. G, Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; pp 519–627.

[20] Work, T. S. *J. Chem. Soc.* **1940**, 1315.