Formation of Nitrilimines and Diazo Compounds from Lithiated and Stannyl Diazo Derivatives: Scope and Mechanism

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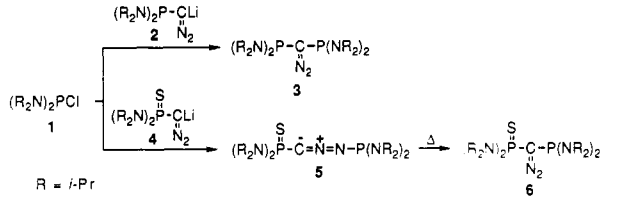
Abstract: The lithium salt of [bis(dicyclohexylamino)phosphanyl]diazomethane (**7**) reacts with bis(diclohexylamino)-chlorophosphane (**8**) leading to a mixture of nitrilimine **9** and diazo derivative **10**, in a 21/4 ratio. The reaction of [bis-(diisopropylamino)thioxophosphoranyl](trimethylstannyl)diazomethane (**11**) with bis(diisopropylamino)chloroborane (**12**) gives *C*-[bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)boryl]nitrilimine (**13**), in 60% yield. Bis(trimethylstannyl)diazomethane (**14**) reacts in polar solvents with 2 equiv of chloroborane **12**, chlorophosphanes **1** and **8**, triphenylmethyl chloride, and trimethylacetyl chloride affording the corresponding nitrilimines **15**, **16**, **9**, and **17** and oxadiazole **26**, respectively, in high yield. In a similar fashion, without solvent, **14** reacts with triisopropylchlorosilane producing nitrilimine **20**. In solution, **14** reacts with triisopropylchlorosilane and with acetyl chloride, leading to diazo derivatives **21** and **27** in 55 and 90% yields. Addition of chlorophosphane **1**, trimethylacetyl chloride, and methanol to (triisopropylsilyl)(trimethylstannyl)diazomethane (**21**) gives rise to *C*-silyl-*N*-phosphanylnitrilimine **22** (70% yield), oxadiazole **23** (34% yield) and (triisopropylsilyl)diazomethane (**24**) (95% yield), respectively. It is clear that steric factors control the stability of nitrilimines, as well as the electrophilic C or N attack, and thus the formation of nitrilimines versus diazo derivatives from metalated diazomethane (metal = lithium or tin).

Introduction

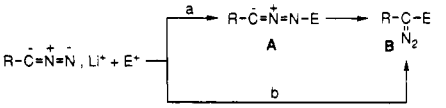
We have shown recently[1] that the reaction of diazo lithium salts with electrophiles led either to diazo compounds or to their thermodynamically less favored nitrilimine isomers.[2] A minor modification to one of the reagents may change dramatically the fate of the reaction. For instance, chlorophosphane **1** reacts with the lithium salt of phosphanyldiazomethane **2** to afford the corresponding substituted diazo compound **3**,[1b,3] whereas, under the same experimental conditions, the lithium salt of the (thioxophosphoranyl)diazomethane analog **4** gives rise to the stable nitrilimine **5**.[1c,f] Lastly, it is important to note that the thermal rearrangement of nitrilimines into their diazo isomers has been well established[1d,4] (Scheme I).

Since it was difficult to predict how substituents would affect the outcome of the reaction, the understanding of the mechanism was of primary interest. It is clear that the formation of nitrilimines results from the attack of the electrophile at the nitrogen end of the diazo lithium salt. From our previous investigations,[1] the diazo isomers seemed to result from a two-step process: the primary formation of nitrilimine A, which undergoes a subsequent isomerization into B (Scheme II, route a). However, the direct attack of the electrophile at the carbon atom of the diazo lithium salt could also explain the formation of the diazo compounds (route b). The former hypothesis would imply that the C- and N-attacks are two competitive reactions. Until now, regardless of the reagents, the concomitant formation of both isomers has never been observed, strongly arguing for the first proposed mechanism (route a).

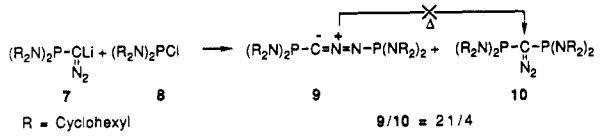
Scheme I



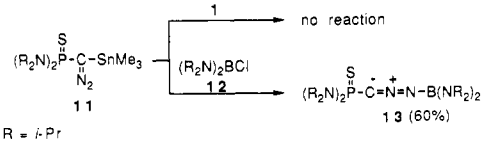
Scheme II



Scheme III



Scheme IV



In this paper, we report the first examples of concomitant formation of both isomers, proving that the formation of diazo derivatives can indeed result from direct attack of the electrophile at the carbon atom of the diazo lithium salt. The factors controlling the electrophilic C- versus N-attack are discussed. The clarification of the mechanism has led to the use of tin diazo compounds as new and efficient precursors for nitrilimines.[5] The scope and mechanism of this new synthetic method are described.

Results

The lithium salt of [bis(dicyclohexylamino)phosphanyl]diazomethane (**7**) reacts in THF, at -80 °C, with bis(dicyclohexylamino)chlorophosphane (**8**), leading to a mixture of nitrilimine **9** and diazo derivative **10**, in a 21/4 ratio (according to ^{31}P NMR spectroscopy). Diazo compound **10** was isolated by

(1) (a) Baceiredo, A.; Bertrand, G.; Sicard, G. *J. Am. Chem. Soc.* **1985**, *107*, 4871. (b) Baceiredo, A.; Igau, A.; Bertrand, G.; Menu, M. J.; Dartiguenave, Y.; Bonnet, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 7868. (c) Menu, M. J.; Desrosiers, P.; Dartiguenave, M.; Dartiguenave, G.; Bertrand, G. *Organometallics* **1987**, *6*, 1822. (d) Granier, M.; Baceiredo, A.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1350. (e) Castan, F.; Baceiredo, A.; Bertrand, G. *Angew. Chem. Int., Ed. Engl.* **1989**, *28*, 1250. (f) Granier, M.; Baceiredo, A.; Dartiguenave, Y.; Menu, M. J.; Bertrand, G. *J. Am. Chem. Soc.* **1990**, *112*, 6277. (g) Castan, F.; Baceiredo, A.; Bigg, D.; Bertrand, G. *J. Org. Chem.* **1991**, *56*, 1801. (h) Arthur, M. P.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1991**, *113*, 5856. (i) Arthur, M. P.; Goodwin, H.; Baceiredo, A.; Dillon, K. B.; Bertrand, G. *Organometallics* **1991**, *10*, 3205. (j) Arthur, M. P.; Baceiredo, A.; Bertrand, G. *Synthesis*, in press.

(2) Moffat, J. B. *J. Mol. Struct.* **1979**, *52*, 275.

(3) Menu, M. J.; Dartiguenave, M.; Dartiguenave, Y.; Bonnet, J. J.; Bertrand, G.; Baceiredo, A. *J. Organomet. Chem.* **1989**, *372*, 201.

(4) (a) Wentrup, C. *Helv. Chim. Acta* **1978**, *61*, 1755. (b) Gleiter, R.; Rettig, W.; Wentrup, C. *Helv. Chim. Acta* **1974**, *57*, 2111. (c) Padwa, A.; Caruso, T.; Nahm, S.; Rodriguez, A. *J. Am. Chem. Soc.* **1982**, *104*, 2865.

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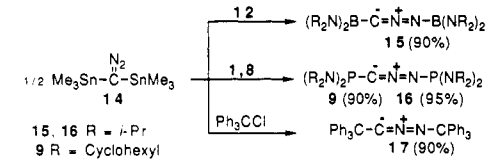
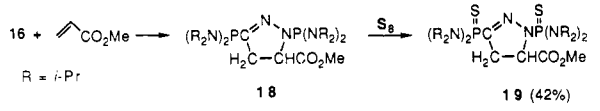
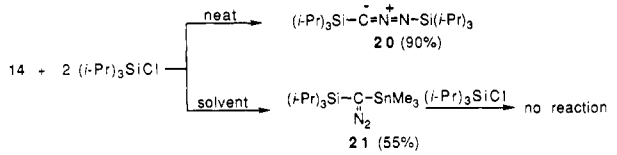
Scheme V



Scheme VI



Scheme VII



column chromatography (10% yield), whereas all attempts to isolate nitrilimine **9**, from this reaction mixture, failed. It is of interest to note that we have not been able to thermally isomerize **9** into **10** (Scheme III).

[Bis(diisopropylamino)thioxophosphoranyl](trimethylstannyl)diazomethane (**11**) is inert against bis(diisopropylamino)chlorophosphane (**1**), but reacts in $CDCl_3$, at 60 °C, with bis(diisopropylamino)chloroborane (**12**), giving *C*-[bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)boryl]nitrilimine (**13**),[1i] in 60% spectroscopic yield (Scheme IV).

Bis(trimethylstannyl)diazomethane (**14**)[6] readily reacts in polar solvents (THF or CH_3CN), at room temperature, with 2 equiv of bis(diisopropylamino)chloroborane (**12**), bis(amino)chlorophosphanes **1** and **8**, and triphenylmethyl chloride to give the corresponding nitrilimines **15**,[1h-j] **16**,[5] **9**, and **17**[5] in near quantitative yields, along with trimethylchlorostannane (Scheme V). When 1 equiv of these electrophiles was used, the same nitrilimines were obtained besides the starting diazo derivative **14**.

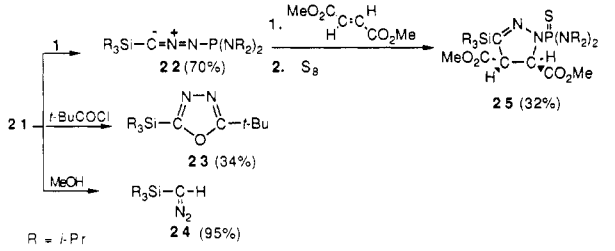
Nitrilimine **15** was characterized by comparison of its spectroscopic data with those of an authentic sample.[1j] Compounds **9** and **16** have been characterized by spectroscopy in solution; furthermore, pyrazoline **19** was isolated in 42% yield after treatment of **16** with methyl acrylate[7] and elemental sulfur (Scheme VI). An X-ray crystal structure study was performed for nitrilimine **17**.[5]

When the reaction of **14** with 2 equiv of triisopropylchlorosilane is carried out without solvent, bis(triisopropylsilyl)nitrilimine (**20**)[1g] is obtained cleanly. The same reaction performed in solution (THF, CH_2Cl_2, or toluene) leads to the formation of (triisopropylsilyl)(trimethylstannyl)diazomethane (**21**), which is stable enough to be purified by distillation (55% yield). Even at elevated temperature in solution or without solvent, **21** does not react with additional triisopropylsilyl chloride (Scheme VII).

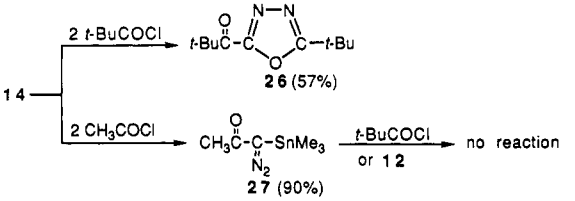
Derivative **21**, however, does react with bis(diisopropylamino)chlorophosphane (**1**) and trimethylacetyl chloride in THF at 40 °C and with methanol at room temperature, giving *C*-(triisopropylsilyl)-*N*-[bis(diisopropylamino)phosphanyl]nitrilimine (**22**) (70% spectroscopic yield), oxadiazole **23** (34% yield), and (triisopropylsilyl)diazomethane (**24**)[1g] (95% yield). Nitrilimine **22** has been characterized by spectroscopy in solution and by its reactivity with dimethyl fumarate; after addition of elemental sulfur, pyrazoline **25** was isolated in 32% yield (Scheme VIII).

Addition of 2 equiv of trimethylacetyl chloride to **14** gives rise to oxadiazole **26** (57% yield), while under the same experimental

Scheme VIII



Scheme IX



conditions, acetyl chloride leads to a mixture of diazo compound **27** (90% yield) and unreacted acyl chloride. Diazo compound **27** is purified by distillation; it is inert toward electrophiles such as trimethylacetyl chloride or bis(diisopropylamino)chloroborane (**12**) (Scheme IX).

Discussion

The first example of concomitant formation of a nitrilimine (**9**) and its isomeric diazo derivative (**10**), found in the reaction of **7** with **8**, coupled with the absence of thermal isomerization of **9** into **10** (Scheme III) clearly demonstrates that competitive C- or N-attack of an electrophile on a diazo lithium salt can occur. This statement is confirmed by the formation of the bis(phosphanyl)diazomethane **3** by the lithium salt route (Scheme I), while the isomeric bis(phosphanyl)nitrilimine **16** (Scheme V) is thermally stable. Comparison of the results in Schemes I and III proves that electronic factors do not control the fate of the reaction, but that a small modification of the steric hindrance of the reagents has a dramatic effect. Indeed, the replacement of the lone pair of **2** by a sulfur atom or of the isopropylamino groups by cyclohexylamino groups totally reverses the diazo derivative/nitrilimine ratio (**3**/**16** = 100/0; **6**/**5** = 0/100; **10**/**9** = 16/84): increasing the steric hindrance favors the formation of nitrilimines.

Considering these results as a whole, it was logical to think that the use of diazo precursors bearing a metal atom larger than lithium would favor formation of nitrilimines; stannyl diazo compounds were potentially good candidates. To check the reactivity of this type of tin–carbon bond, (stannyl)(thioxophosphoranyl)diazomethane derivative **11** was allowed to react with different electrophiles (Scheme IV). Derivative **11** is less reactive than its lithium analog **4**, but does lead to the formation of nitrilimine **13** with chloroborane **12**. Note that this nitrilimine **13** was already obtained by the lithium salt method.[1i] Then, the question arises as to whether bis(trimethylstannyl)diazomethane (**14**) would act as a CNN^{2-}-transferring agent and thus would allow one-step syntheses of nitrilimines, especially those not accessible by the diazo lithium salt route. The results summarized in Scheme V clearly demonstrate these possibilities. The formation of bis(boryl)nitrilimine **15** in high yield shows the efficiency of the method. By the lithium salt route, **16** was not available, while **9** was obtained as a mixture with its diazo isomer **10**. The stannyldiazomethane precursor only leads to nitrilimine, demonstrating the high selectivity of the method. The most striking result is certainly the preparation of derivative **17**, the first stable purely organic nitrilimine.[5] Compound **17** is, as a solid, indefinitely air stable and exhibits typical 1,3-dipolar reactivity[7] as illustrated by Scheme X. It is important to note that the reactions leading to nitrilimines **9** and **15**–**17** are very fast and that no monosubstituted intermediates can be observed.

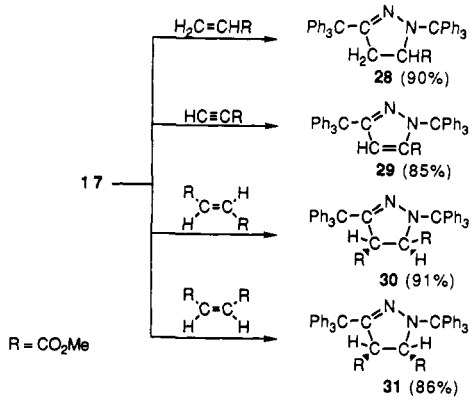
The experiments performed with triisopropylchlorosilane (Scheme VII) show that **14** can act not only as a nitrilimine but also as a diazo precursor. The dramatic difference observed in

(5) For a preliminary account see: Rêau, R.; Veneziani, G.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 439.

(6) Lappert, M. F.; Lorberth, J.; Poland, J. S. *J. Chem. Soc. A* **1970**, 2954.

(7) For reviews concerning 1,3-dipolar cycloadditions involving nitrilimines, see: Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565. Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633. Caramella, P.; Grünanger, P. *1,3 Dipolar Cycloaddition Chemistry*; Wiley: New York, 1984.

Scheme X



the reaction of **14** with triisopropylchlorosilane, with and without solvent, is of primary interest (Scheme VII). Since (silyl)(stannyl)diazomethane **21** does not react with triisopropylchlorosilane, it is clear that **21** is not the intermediate leading to nitrilimine **20**. Thus, the first step is certainly, for both experimental conditions, a N-silylation giving rise to *C*-stannyl-*N*-silylnitrilimine **32**. Then, in the absence of solvent, **32** undergoes a substitution reaction by another molecule of chlorosilane affording bis(silyl)nitrilimine **20**, while in the presence of a solvent, nitrilimine **32** has enough time to rearrange into the isomeric diazo compound **21**.

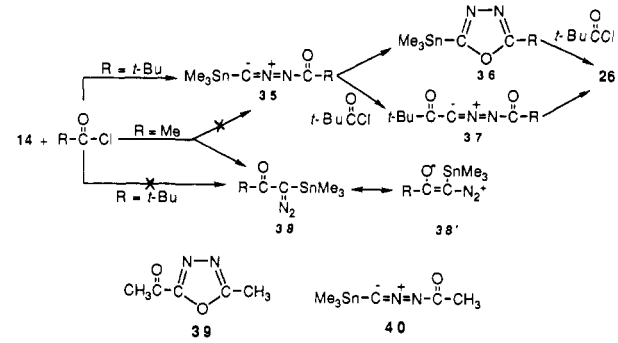
$$\underset{\mathbf{32}}{Me_3SnC^-{=}N^+{=}NSi(i\text{-}Pr)_3}$$

These results show that electrophilic attack at stannyl diazo compounds takes place at the nitrogen end, but it was of interest to know if, as for the lithium salts, small electrophiles could also react at carbon, directly leading to the diazo derivatives. The results observed with (silyl)(stannyl)diazomethane **21** (Scheme VIII) do not give a definite answer. Not surprisingly, reaction with a sterically hindered electrophile (chlorophosphane **1**) produces the nitrilimine **22**. With trimethylacetyl chloride, oxadiazole **23** is formed. This heterocycle comes from *N*-acylnitrilimine **33**, which undergoes a well-exemplified 1,5-electrocyclization.[8] The formation of (triisopropylsilyl)diazomethane (**24**) could result from a C-protonation, but the transient intermediacy of a N-unsubstituted nitrilimine **34** cannot be ruled out.

$$\underset{\mathbf{33}}{(i\text{-}Pr)_3SiC^-{=}N^+{=}NC(O)t\text{-}Bu} \qquad \underset{\mathbf{34}}{(i\text{-}Pr)_3SiC^-{=}N^+{=}NH}$$

The definitive proof for a C-attack of an electrophile on a stannyl diazo compound comes from the comparison of the reactivity of **14** with two different acyl chlorides (Scheme IX). With trimethylacetyl chloride, formation of oxadiazole **26** proves primary formation of *C*-stannyl-*N*-acylnitrilimine **35**. Then, this *N*-acylnitrilimine **35** undergoes either a 1,5-electrocyclization to stannyloxadiazole **36** and a subsequent acylation or a substitution reaction leading to the transient bis(acyl)nitrilimine **37** followed by an electrocyclization (Scheme XI). The first step of this reaction cannot be a C-acylation giving the (acyl)(stannyl)diazomethane **38**, considering the nonreactivity of the analogous diazo compound **27**. On the other hand, when a small acyl chloride (acetyl chloride) is used, oxadiazole **39** is not obtained, but instead formation of (acyl)(stannyl)diazomethane **27** is observed, which rules out the possible primary formation of *N*-acylnitrilimine **40**. Finally, the absence of reactivity of (acyl)(stannyl)diazomethane **27**, even at elevated temperature, is due to the strong interaction between the diazo and the carbonyl groups (favored by coordination of the oxygen to tin[9]) making the diazonium resonance form 38′ of great importance.[10]

Scheme XI



Conclusion

The results reported in this paper proved that C- and N-attacks of electrophiles on metalated diazomethane are two competitive processes. Steric hindrance of both reagents is the factor controlling the ratio of both isomers. The metal can have a dramatic influence on the selectivity of the reaction as illustrated by the ratio nitrilimine **16**/diazo derivative **3**, obtained from diazo lithium salt **2** (0/100) and bis(stannyl)diazomethane **14** (100/0).

The stannyl diazo derivatives allow the straightforward synthesis of a variety of symmetrically or unsymmetrically substituted nitrilimines as well as the one-step synthesis of heterocycles. The experimental conditions used are very mild, and the trimethylstannyl chloride formed in these reactions is easily removed by sublimation (10^{-2} mmHg, room temperature). Bis(trimethylstannyl)diazomethane (**14**) acts as a safe "CNN^{2-}"-transferring agent, in contrast with potential analogs such as the bis(mercuro)-[11] or bis(silver)diazomethane salts,[12] which are known to be explosive.

In the late 1950s, Huisgen[13] reported evidence for the transient formation of nitrilimines. In the beginning of the 1980s, these 1,3-dipoles were spectroscopically characterized in matrices at 85 K by several groups[14] and in the gas phase by Bock.[15] The first isolated nitrilimine (**5**) appeared in 1988 as a laboratory curiosity; now it is clear that a wide variety of stable nitrilimines, including purely organic compounds, can be easily prepared in multiple-gram quantities.

Nitrilimines must now be considered as easily available building blocks.

Experimental Section

All experiments were performed in an atmosphere of dry argon. Melting points are uncorrected. ^1H, ^{13}C, ^{31}P, ^{14}N, ^{119}Sn, and ^{29}Si NMR spectra were recorded on Brucker AC80, AC200, or WM250 spectrometers. ^1H, ^{13}C, and ^{29}Si NMR chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P, ^{14}N, and ^{119}Sn NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4, neat $MeNO_2$, and Me_4Sn, respectively. Infrared spectra were recorded on a Perkin-Elmer FT-IR 1725 X spectrometer. Mass spectra were obtained on a Ribermag R10 10E instrument. Liquid chromatography was performed on silica gel or neutral alumina. Conventional glassware was used.

Synthesis of Bis[bis(dicyclohexylamino)phosphanyl]diazomethane (10). To a THF solution (10 mL) of [bis(dicyclohexylamino)phosphanyl]diazomethane[13] (0.86 g, 2 mmol), at −78 °C, was added dropwise a stoichiometric amount of BuLi in hexane. After the mixture was stirred for 30 min at −78 °C, a THF (10 mL) solution of bis(dicyclohexylamino)-

(8) For a review on 1,5-electrocyclizations involving nitrilimines, see: Taylor, E. C.; Turchi, I. J. *Chem. Rev.* **1979**, *79*, 181.

(9) (a) Lorberth, J. *J. Organomet. Chem.* **1968**, *15*, 251. (b) Lorberth, J.; Shin, S. H.; Donath, H.; Wocaldo, S.; Massa, W. *J. Organomet. Chem.* **1991**, *407*, 167.

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(17) Horchler von Locquenghien, K.; Réau, R.; Bertrand, G. *J. Chem. Soc., Chem. Commun.* **1991**, 1192.

chlorophosphane (**8**)[16] (0.85 g, 2 mmol) was added. The solution was allowed to warm to room temperature, and the solvent was removed under vacuum. The residue was treated with pentane and filtered. According to NMR data, nitrilimine **9** (see after) and diazo derivative **10** were obtained in a 21/4 ratio. After purification on neutral alumina (hexane/ether, 98/2, R_f = 0.6) and crystallization in pentane at −20 °C, **10** was obtained as an orange solid (0.16 g, 10 % yield): mp 139–140 °C; ^{31}P NMR (C_6D_6) +67.4; ^{13}C NMR (C_6D_6) 25.82, 26.80, 27.06 (s, CH_2), 35.11 (t-like, J_{CP} = 5.0 Hz, NCHCH_2), 41.28 (t, J_{CP} = 73.0, CN_2), 57.88 (t-like, J_{CP} = 5.5 Hz, CH); IR (THF) 2000 and 2014 cm^{-1} (CN_2). Anal. Calcd for $C_{49}H_{88}N_6P_2$: C, 71.49; H, 10.77; N, 10.21. Found: C, 71.61; H, 10.95; N, 10.70.

Synthesis of [Bis(diisopropylamino)thioxophosphoranyl](trimethylstannyl)diazomethane (11). To a THF solution of [bis(diisopropylamino)thioxophosphoranyl]diazomethane[1f] (0.61 g, 2 mmol), at −78 °C, was added dropwise a stoichiometric amount of BuLi in hexane. After the mixture was stirred for 30 min at −78 °C, a THF solution (10 mL) of trimethylstannyl chloride (0.40 g, 2 mmol) was added. The solution was allowed to warm to room temperature, and the solvent was removed under vacuum. The residue was treated with pentane and filtered. After evaporation of pentane, **11** was obtained in analytically pure form as a yellow oil (0.89 g, 95% yield): ^{31}P NMR (C_6D_6) +65.9 ($J_{P^{117}Sn}$ = 107 Hz, $J_{P^{119}Sn}$ = 111 Hz); ^{13}C NMR (C_6D_6) −4.72 (s, $J_{C^{117}Sn}$ = 364.4 Hz, $J_{C^{119}Sn}$ = 381.0 Hz, $SnCH_3$), 23.80 (d, J_{PC} = 2.5 Hz, CHCH_3), 24.55 (d, J_{PC} = 2.6 Hz, CHCH_3), 41.46 (d, J_{PC} = 132.2 Hz, CN_2), 47.86 (d, J_{PC} = 5.0 Hz, CH); ^{1}H NMR (C_6D_6) 0.45 (s, $J_{H^{117}Sn}$ = 54.4 Hz, $J_{H^{119}Sn}$ = 56.8 Hz, $SnCH_3$, 9 H), 1.28 (d, J_{HH} = 6.8 Hz, 12 H, CHCH_3), 1.36 (d, J_{HH} = 6.8 Hz, 12 H, CHCH_3), 3.77 (m, J_{PH} = 17.3 Hz, J_{HH} = 6.9 Hz, 4 H, CH); ^{119}Sn NMR ($CDCl_3$) +23.8 ($J_{P^{119}Sn}$ = 110 Hz); ^{14}N NMR ($CDCl_3$) −134.4 ($\nu_{1/2}$ = 180 Hz, C*N*N)[17]; IR (THF) 2025 cm^{-1} (CN_2). Anal. Calcd for $C_{16}H_{37}N_4PSSn$: C, 41.12; H, 7.99; N, 12.00. Found: C, 41.61; H, 8.12; N, 11.82.

Reaction of 11 with Bis(diisopropylamino)chloroborane (12). To a $CDCl_3$ solution (2 mL) of **11** (0.3 g, 0.64 mmol) was added at room temperature an excess of **12** (0.2 g, 0.8 mmol). The mixture was heated at 60 °C, and the reaction was monitored by ^{31}P NMR. Nitrilimine **13**, obtained in a 60 % spectroscopic yield, was characterized in solution by comparison of the spectroscopic data with those of an authentic sample.[1i]

General Procedure for the Reaction of 1, 8, 12, Acyl Chlorides, and Triisopropylchlorosilane with Bis(trimethylstannyl)diazomethane (14). A THF solution (10 mL) of electrophile (3 mmol) was added dropwise, at room temperature, to a solution of **14** (0.55 g, 1.5 mmol) in THF (5 mL). The solution was stirred for 1 h, and the reaction was monitored by IR. After the solvent and trimethylchlorostannane were removed under vacuum (overnight, room temperature, 10^{-2} mmHg), the nitrilimine or the diazo compound was obtained.

Bis[bis(dicyclohexylamino)phosphanyl]nitrilimine (9) was characterized only in solution: ^{31}P NMR (THF) +52.0, +100.0 (J_{PP} = 9.1 Hz); ^{13}C NMR (C_6D_6) 25.93–27.10 (m, CH_2), 34.04–34.62 (m, CH_2), 35.18 (d, J_{PC} = 5.2 Hz, CHCH_2), 35.68 (d, J_{PC} = 8.4 Hz, CHCH_2), 55.13 (d, J_{PC} = 9.7 Hz, CH), 58.27 (d, J_{PC} = 9.3 Hz, CH), 64.40 (d, J_{PC} = 72.8 Hz, CNN); ^{1}H NMR (C_6D_6) 0.80–1.84 (m, 80 H, CH_2), 3.04 (m, 4 H, NCH), 3.21 (m, 4 H, NCH); IR (THF) 2047 cm^{-1} (br, CNN).

Bis[bis(diisopropylamino)boryl]nitrilimine (15) and bis(triisopropylsilyl)nitrilimine (20) were obtained by distillation. Their physical and spectroscopic data were compared to those of authentic samples (**15**[1j] and **20**[1e]).

Bis[bis(diisopropylamino)phosphanyl]nitrilimine (16) was obtained as an orange oil: ^{31}P NMR (THF) +45.5, +96.0 (J_{PP} = 9.0 Hz); ^{13}C NMR (C_6D_6) 24.10 (d, J_{PC} = 9.7 Hz, CH_3), 24.45 (d, J_{PC} = 5.7 Hz, CH_3), 24.87 (d, J_{PC} = 6.0 Hz, CH_3), 25.39 (d, J_{PC} = 8.9 Hz, CH_3), 46.08 (d, J_{PC} = 11.9 Hz, CH), 49.50 (d, J_{PC} = 11.7 Hz, CH), 63.28 (d, J_{PC} = 62.5 Hz, CNN); ^{1}H NMR (C_6D_6) 1.05 (d, J_{HH} = 6.8 Hz, 12 H, CH_3), 1.17 (d, J_{HH} = 6.6 Hz, 12 H, CH_3), 1.23 (d, J_{HH} = 6.8 Hz, 12 H, CH_3), 1.35 (d, J_{HH} = 6.6 Hz, 12 H, CH_3), 3.34 (sept d, J_{HH} = 6.6 Hz, J_{PH} = 11.4 Hz, 4 H, CH), 3.64 (sept d, J_{HH} = 6.8 Hz, J_{PH} = 10.7 Hz, 4 H, CH); ^{14}N NMR ($CDCl_3$) −191.9 ($\nu_{1/2}$ = 250 Hz, C*N*N) −320 ($\nu_{1/2}$ = 1300 Hz, i-Pr_2N); IR (THF) 2047 cm^{-1} (br, CNN).

Reaction of 16 with Methyl Acrylate. To a THF solution (2 mL) of **16** (0.40 g, 0.89 mmol) was added, at room temperature, a stoichiometric amount of methyl acrylate (0.07 g, 0.81 mmol). The reaction was monitored by ^{31}P NMR, and the adduct **18** was characterized in solution: ^{31}P NMR (THF) +75.0, +40.9 (J_{PP} = 3.8 Hz). After the solution was stirred for 2 h with an excess of elemental sulfur, the mixture was filtered and **19** was purified by crystallization in cold hexane as a colorless solid. Its spectroscopic data were compared to those of an authentic sample.[1f]

Synthesis of Bis(triphenylmethyl)nitrilimine (17). An acetonitrile solution (4 mL) of **14** (0.28 g; 0.76 mmol) was added dropwise to 2 equiv of triphenylmethyl chloride (0.42 g, 1.51 mmol) in acetonitrile (6 mL), at −30 °C. The solution was stirred for 1 h at −30 °C; **17** precipitated as a pale yellow solid, which was washed several times with acetonitrile and allowed to stand overnight at room temperature in vacuo to eliminate trimethylchlorostannane. Nitrilimine **17** was recrystallized from THF/Et_2O as pale yellow crystals (0.36 g, 90%): mp 60 °C dec. As a solid, **17** is air stable, but it slowly decomposes in solution above −20 °C: ^{13}C NMR ($CDCl_3$, 243 K) 60.71 (s, Ph_3CC), 76.26 (s, $NCPh_3$), 85.5 (s, CNN), 126.48, 127.17, 127.66, 128.04, 128.53, 128.68 (s, CH_{arom}), 142.43 (s, C_i), 144.4 (s, C_i); ^{1}H NMR ($CDCl_3$, 243 K) 6.5–7.5 (m); ^{14}N NMR ($CDCl_3$, 253 K) −182.1 ($\nu_{1/2}$ = 280 Hz, C*N*N); IR (THF) 2052 cm^{-1} (br, CNN). Anal. Calcd for $C_{39}H_{30}N_2{\cdot}0.8Et_2O$: C, 86.49; H, 6.53; N, 4.78. Found: C, 86.57; H, 6.46; N, 4.68. Nitrilimine **17** reacted with methyl acrylate, methyl propiolate, dimethyl fumarate, or dimethyl maleate to give the corresponding five-membered rings **28–31**. To a THF solution (10 mL) of nitrilimine **17** (0.35 g, 0.66 mmol), at −30 °C, was added a stoichiometric amount of dipolarophile. The mixture was allowed to warm to room temperature, and the solvent was then removed under vacuum. After being washed several times with pentane and dried in vacuo, adducts **28–31**[5] were obtained as white solids. **28**: 0.36 g, 90%; mp 214–215 °C; ^{13}C NMR ($CDCl_3$) 42.19 (s, CH_2), 51.73 (s, OCH_3), 61.10 (s, CCPh_3), 62.76 (s, CH_{ring}), 78.58 (s, $NCPh_3$), 125.97, 126.02, 127.12, 127.15, 129.62, 130.15 (s, C_{arom}), 143.10 (s, C_i), 143.8 (s, C_i) 156.46 (s, C=N), 174.20 (s, CO); ^{1}H NMR ($CDCl_3$) ABX system 2.18 (dd, J_{HAHX} = 11.4 Hz, J_{HAHB} = 16.8 Hz, 1 H, CH_A), 2.6 (dd, J_{HBHX} = 9.3 Hz, J_{HAHB} = 16.8 Hz, 1 H, CH_B), 3.47 (s, 3 H, OCH_3), 3.89 (dd, J_{HAXB} = 9.3 Hz, J_{HXHA} = 11.4 Hz, 1 H, CH_X), 6.96–7.46 (m, H_{arom}, 30 H); IR (THF) 1749 cm^{-1} (CO), 1597 cm^{-1} (C=N); mass spectrum (E/I), *m/e* 612. Anal. Calcd for $C_{43}H_{36}N_2O_2$: C, 84.28; H, 5.92; N, 4.57. Found: C, 83.75; H, 6.12; N, 4.52. **29**: 0.32 g, 85%; mp 172–173 °C; pentane/Et_2O, 90/10, R_f = 0.31; ^{13}C NMR ($CDCl_3$) 51.28 (s, OCH_3), 60.08 (CCPh_3), 80.78 (s, $NCPh_3$), 115.09 (s, C_{ring}), 129.95, 126.82, 127.11, 127.74, 130.11, 130.54, (s, C_{arom}), 134.61 (s, CH_{ring}), 143.02 (s, C_i), 146.42 (s, C_i), 155.06 (s, C=N), 159.20 (s, CO); ^{1}H NMR ($CDCl_3$) 3.21 (s, 3 H, OCH_3), 6.45 (s, 1 H, CH_{ring}), 7.04–7.25 (m, H_{arom}); IR (THF) 1743 cm^{-1} (CO); mass spectrum, 611 (M + 1). Anal. Calcd for $C_{43}H_{34}N_2O_2$: C, 84.56; H, 5.61; N, 4.59. Found: C, 84.49; H, 5.52; N, 4.60. **30**: 0.40 g, 91%; mp 180–182 °C; pentane/Et_2O, 90/10, R_f = 0.49; ^{13}C NMR ($CDCl_3$) 51.51 (s, OCH_3), 52.02 (s, OCH_3), 59.83 (s, CH_{ring}), 62.02 (s, CCPh_3), 67.71 (s, CH_{ring}), 78.48 (s, $NCPh_3$), 125.09, 126.20, 127.06, 127.21, 129.83, 130.53, (s, C_{arom}), 142.72 (s, C_i), 143.95 (s, C_i), 150.47 (s, C=N), 168.54 (s, CO), 172.55 (s, CO); ^{1}H NMR ($CDCl_3$) 2.85 (s, OCH_3), 3.31 (s, OCH_3), 4.11 (d, J_{HH} = 11.4 Hz, 1 H, CH_{ring}), 4.30 (d, J_{HH} = 11.4 Hz, 1 H, CH_{ring}), 6.98–7.51 (m, 30 H, H_{arom}); IR ($CDCl_3$) 1742 (CO), 1596 (C=N); mass spectrum, 671 (M + 1). Anal. Calcd for $C_{45}H_{38}N_2O_4$: C, 80.57; H, 5.71; N, 4.17. Found: C, 80.63; H, 5.78; N, 4.21. **31**: 0.38 g, 86%; mp 177 °C dec; pentane/Et_2O, 90/10, R_f = 0.68; ^{13}C NMR ($CDCl_3$) 51.58 (s, OCH_3), 51.84 (s, OCH_3), 57.54 (s, CH_{ring}), 62.05 (s, CCPh_3), 67.57 (s, CH_{ring}), 78.19 (s, $NCPh_3$), 125.09, 126.20, 127.01, 127.27, 129.85, 130.83, (s, C_{arom}), 142.44 (s, C_i), 143.49 (s, C_i), 155.56 (s, C=N), 168.24 (s, CO), 169.58 (s, CO); ^{1}H NMR ($CDCl_3$) 3.19 (s, OCH_3), 3.32 (s, OCH_3), 3.53 (d, J_{HH} = 10.4 Hz, 1 H, CH_{ring}), 4.22 (d, J_{HH} = 10.4 Hz, 1 H, CH_{ring}), 6.96–7.45 (m, 30 H, H_{arom}); IR ($CDCl_3$) 1742 (CO), 1596 (C=N); mass spectrum, 671 (M + 1). Anal. Calcd for $C_{45}H_{38}N_2O_4$: C, 80.57; H, 5.71; N, 4.17. Found: C, 80.63; H, 5.78; N, 4.21.

(Triisopropylsilyl)(trimethylstannyl)diazomethane (21) was obtained by distillation as a yellow liquid (0.29 g, 55%): bp 80 °C (5×10^{-2} mmHg); ^{13}C NMR ($CDCl_3$) −7.32 (s, $J_{C^{117}Sn}$ = 347.7 Hz, $J_{C^{119}Sn}$ = 364.0 Hz, $SnCH_3$), 7.89 (s, $J_{C^{117}Sn}$ = 214.6 Hz, $J_{C^{119}Sn}$ = 226.4 Hz, CN_2), 12.43 (s, CH), 18.53 (s, CHCH_3); ^{1}H NMR ($CDCl_3$) 0.38 (s, $J_{H^{117}Sn}$ = 52.9 Hz, $J_{H^{119}Sn}$ = 55.0 Hz, 9 H, $SnCH_3$), 1.16 (m, 21 H, *i*-Pr); ^{14}N NMR ($CDCl_3$) −129.2 ($\nu_{1/2}$ = 162 Hz, C*N*N); ^{119}Sn NMR ($CDCl_3$) +42.56; ^{29}Si NMR ($CDCl_3$) +8.8; IR (THF) 2015 cm^{-1} (CN_2). Anal. Calcd for $C_{13}H_{30}N_2SiSn$: C, 43.23; H, 8.37; N, 7.75. Found: C, 44.15; H, 8.09; N, 7.98.

Synthesis of *C*-(Triisopropylsilyl)-*N*-[bis(diisopropylamino)phosphanyl]nitrilimine (22). A THF solution (10 mL) of **1** (0.40 g, 1.5 mmol) was added dropwise to **21** (0.53 g, 1.5 mmol) in THF (5 mL). After the solution was stirred for 1 h at 40 °C, **22** (70% spectroscopic yield) was characterized in solution: ^{31}P NMR (THF) +101.4; IR (THF) 2099 cm^{-1} (br, CNN). To this THF solution was added an excess of dimethyl fumarate (0.29 g, 2 mmol). The (phosphanyl)pyrazoline was characterized in solution: ^{31}P NMR (THF) 71.9; IR (THF) 1732 cm^{-1} (CO). To this THF solution was added an excess of elemental sulfur. After the solution was stirred overnight at room temperature, the excess sulfur was filtered off, and the solvent was evaporated. Pyrazoline **25** was isolated by column chromatography (hexane/Et_2O, 80/20, R_f = 0.48) as a colorless oil (0.29 g, 32%): ^{31}P NMR ($CDCl_3$) +59.2; ^{13}C NMR ($CDCl_3$) 11.49 (s, SiCH), 18.29, 18.36 (s, SiCHCH_3), 23.02 (d, J_{PC} = 3.0 Hz, NCHCH_3), 23.63 (d, J_{PC} = 3.5 Hz, NCHCH_3), 24.05 (m, NCHCH_3), 47.06 (d, J_{PC} = 5.6 Hz, NCH), 47.56 (d, J_{PC} = 6.1 Hz, NCH), 52.08

(s, CH_3O), 52.25 (s, CH_3O), 61.01 (d, J_{PC} = 5.6 Hz, CH_{ring}), 64.19 (d, J_{PC} = 13.0 Hz, NCH_{ring}), 148.56 (d, J_{PC} = 8.3 Hz, C=N), 169.62 (s, CO), 171.77 (s, CO); ^1H NMR ($CDCl_3$) 1.06 (m, 21 H, *i*-Pr_3Si), 1.33 (m, J_{HH} = 7.0 Hz, 24 H, CH_3), 3.69 (s, CH_3O, 3 H), 3.71 (s, CH_3O, 3 H), 3.77 (d, J_{HH} = 5.6 Hz, 1 H, CH_{ring}), 4.15 (sept d, J_{PH} = 15.7 Hz, J_{HH} = 7.0 Hz, 4 H, NCH), 5.10 (dd, J_{PH} = 2.0 Hz, J_{HH} = 5.6 Hz, 1 H, CH_{ring}); IR (THF) 1737 cm^{-1} (CO).

Synthesis of Oxadiazole 23. A THF solution (10 mL) of **21** (0.33 g, 0.95 mmol) was added dropwise to trimethylacetyl chloride (0.12 g, 0.95 mmol) in THF (5 mL). After the solution was stirred for 1 h at 40 °C, the solvent was removed under vacuum, and **23** was isolated by column chromatography (hexane/Et_2O, 80/20, R_f = 0.44) as a pale yellow oil (0.09 g, 34%): ^{13}C NMR ($CDCl_3$) 12.1 (s, $CHCH_3$), 17.51 (s, $CHCH_3$), 26.39 (CCH_3), 31.99 (s, CCH_3), 167.91 (s, C=N), 175.95 (s, C=N); ^1H NMR ($CDCl_3$) 1.09–1.28 (s, 21 H, *i*-Pr), 1.39 (s, 9 H, CCH_3); IR (THF) 1561 cm^{-1} (C=N); mass spectrum, *m/e* 283 (M + 1). Anal. Calcd for $C_{15}H_{30}N_2OSi$: C, 63.77; H, 10.70; N, 9.91. Found: C, 64.15; H, 10.19; N, 9.78.

Reaction of 21 with Methanol. To a THF solution (10 mL) of **21** (0.31 g, 0.84 mmol) was added an excess of methanol (0.5 mL). After evaporation of the solvent, **24** was obtained by distillation as a yellow liquid (0.16 g, 95%): bp 90–100 °C (5×10^{-2} mmHg). Its spectroscopic data were compared to those of an authentic sample.[1g]

Oxadiazole 26 was obtained by column chromatography (hexane/Et_2O, 85/15, R_f = 0.52) as a white solid (0.18 g, 57%): mp 94 °C; ^{13}C NMR ($CDCl_3$) 26.30 (s, CH_3), 27.94 (s, CH_3), 32.48 (s, CCH_3), 44.36 (s, C(O)CCH_3), 159.50 (C=N), 174.2 (C=N), 192.56 (CO); ^1H NMR ($CDCl_3$) 1.43 (s, 9 H, CH_3), 1.45 (s, 9 H, CH_3); IR (THF) 1702 cm^{-1} (CO), 1546 cm^{-1} (C=N); mass spectrum, *m/e* 211 (M + 1). Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 63.09; H, 8.72; N, 13.22.

Acetyl(trimethylstannyl)diazomethane (27) was obtained by distillation as a yellow liquid (0.33 g, 90%): bp 40 °C (5×10^{-2} mmHg). In solution, **27** was stable for weeks, but decomposed when pure: ^{13}C NMR ($CDCl_3$) −8.0 (s, $J_{C^{117}Sn}$ = 365.6 Hz, $J_{C^{119}Sn}$ = 379.2 Hz, $SnCH_3$), 25.9 (s, CH_3), 196.5 (s, CO), the CN_2 carbon atom was not observed; ^1H NMR ($CDCl_3$) 0.37 (s, $J_{H^{117}Sn}$ = 55.8 Hz, $J_{H^{119}Sn}$ = 58.1 Hz, 9 H, $SnCH_3$), 2.24 (s, 3 H, CH_3); ^{119}Sn NMR ($CDCl_3$) +25.6; ^{14}N NMR (C_6D_6) −130.8 ($\nu_{1/2}$ = 85 Hz, C*N*N) −49.1 ($\nu_{1/2}$ = 770 Hz, CN*N*); IR (THF) 2053 cm^{-1} (CN_2), 1615 cm^{-1} (CO).

Electrochemical Kinetic Discrimination of the Single-Electron-Transfer Events of a Two-Electron-Transfer Reaction: Cyclic Voltammetry of the Reduction of the Bis(hexamethylbenzene)ruthenium Dication

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Abstract: The electrochemical reduction of $[(\eta^6\text{-}C_6Me_6)_2Ru][BF_4]_2$ has been shown to occur in two one-electron steps, each manifesting solvent-dependent formal potentials. The heterogeneous charge-transfer kinetics varied with electrode material. Cyclic voltammetry (CV) was found to be sensitive to homogeneous reactions which occurred both within the electrode reaction layer and in the bulk of solution. Whereas the reduction waves of $(C_6Me_6)_2Ru^{2+/+/0}$ were resolved in CH_2Cl_2 and separated by −0.14 V ($E^\circ_2 - E^\circ_1$, E°_2 = −1.45 V vs Fc/Fc^+), only a single two-electron wave was observed in CH_3CN because of a negative shift of E°_1 with respect to E°_2 ($E^\circ_2 - E^\circ_1$ = +0.03 V, E°_2 = −1.40 V). Both reductions displayed Nernstian behavior at Hg electrodes. However, the Ru(I/0) couple showed quasireversible charge-transfer kinetics at Pt disk electrodes. At Pt, the two-electron wave was found to split into its one-electron components over a range of sweep rates which varied with analyte concentration. The Ru(I) complex was also subject to a follow-up reaction having a rate constant of 1.0 s^{-1}. Detailed explicit finite difference simulations of the CV curves allowed solution of the electron-transfer parameters for the two one-electron couples in CH_3CN at Pt. The average values from 15 simulations over a scan rate range of 0.4–100 V s^{-1} and a concentration range of 0.50–1.3 mM were as follows: Ru(II/I), E°_1 = −1.43 V, $k_{s1} \geq 2$ cm s^{-1}; Ru(I/0), E°_2 = −1.40 V, $k_{s2} = 4.5 \times 10^{-4}$ cm s^{-1}, α_{02} = 0.50, $d\alpha_2/dE$ = 0.22 V^{-1}. The equilibrium constant and rate constant for the disproportionation reaction 2Ru(I) ⇌ Ru(II) + Ru(0) were 2.0 and 6.3×10^4 M^{-1} s^{-1}, respectively. The diffusion coefficient of the Ru(II) complex was only about 0.45 times that of the Ru(0) complex. This redox system obeyed an $E_{rev}E_{qrev}$ model down to experiment times of 10 μs. This is believed to be the first recognized example of kinetic discrimination between one-electron processes of a two-electron EE wave.

Introduction

Multielectron-transfer reactions which proceed without detectable concentrations of one-electron intermediates are important in a variety of synthetic, catalytic, and biological contexts.[1-5] Although there exists relatively limited knowledge of the mechanisms of these complex reactions,[6] electrochemistry can provide some information.[7,8] For example, well-known criteria allow diagnosis of two-electron processes in which each one-electron transfer[9,10] is Nernstian. When $E^\circ_2 \gg E^\circ_1$ (eqs 1 and 2), the couple

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