pyridine interaction features a Ta–C(1) bond of 2.126 (9) Å and Ta–N bond of 1.966 (6) Å, while C(2) and C(5) are clearly out of bonding range (2.99 (1) Å and 3.159 (8) Å from Ta, respectively). Unlike the related structure of (silox)$_3$Ta(η^2(*N*,*C*)-NC$_5$H$_5$)[9] (silox = ^{t}Bu$_3$SiO), a clear 1,3-diene π localization is not evident in **5**.[21] The pyridine is far from planar: the severe distortion (perhaps sterically enhanced) appears to be toward a twist-boat conformation. Ta–N–C(5) = 140.3 (5)° and Ta–C(1)–C(2) = 111.5 (6)° while the dihedral angle between the best pyridine plane and the Ta–(*N*,*C*) plane is 117.6 (5)°. A short Ta–N bond in conjunction with the NMR data[16] fully supports the η^2-(*N*,*C*) mode of bonding as in (silox)$_3$Ta(η^2(*N*,*C*)-NC$_5$H$_5$),[9] rather than an η^2-(*C*,*C*) mode reported in the lutidine complex [(η^2-lutidine)Os(NH$_3$)$_5$]$^{2+}$.[10]

The structure of **5** suggests that a metal–ligand π interaction (dπ → pπ^*) is preferred over the rather inefficient δ back-bonding (dδ → arene δ^* (arene π^* LUMO) as in **3**)[13,22] to allow the metal to attain its highest oxidation state. No intermediates are observed (by ^{1}H NMR) in the rearrangement of **4** to **5**; thus, whether a transient η^6-pyridine or N-metallacycloimine (TaN=CCMe$_3$CH=CCMe$_3$CH=CCMe$_3$) is involved is unknown. Since the tri-*tert*-butylbenzene ligand coordinates η^6 in complex **3**, it is unlikely that *steric* constraints are inducing an incipient η^6-tri-*tert*-butylpyridine ligand to slip to the observed η^2 form in **5**. The η^2 coordination results in a disruption of the pyridine's aromaticity, severely distorts the ligand, and extracts a high energetic price,[23] but one that seems to be more than recovered in the tantalum–nitrogen interaction. Additionally, compounds related to **5** may be relevant to C–H bond activation; intermediate η^2-(*N*,*C*) pyridine species may be implicated prior to pyridyl (η^2(*N*,*C*)-NC$_5$H$_4$) formation[24] and related pyridine C$_\alpha$ functionalizations.[25]

Acknowledgment. Support from the U.S. Army Research Office (Short Term Innovative Research Program) and the Department of Chemistry, University of Arizona, are gratefully acknowledged. We thank Dr. A. Rai-Chauduri for obtaining the PES spectrum of **5**.

Supplementary Material Available: Analytical and spectroscopic data for compounds **1–4** and tables of crystal data and data collection parameters, atomic positional and thermal parameters, bond distances, and bond angles for (η^2(*N*,*C*)-2,4,6-NC$_5$H$_2$^{t}Bu$_3$)Ta(O-2,6-C$_6$H$_3$^{i}Pr$_2$)$_2$Cl (5 pages). Ordering information is given on any current masthead page.

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(20) A dark red irregular crystal of (η^2(*N*,*C*)-2,4,6-NC$_5$H$_2$^{t}Bu$_3$)Ta(DIPP)$_2$Cl (approximate dimensions 0.30 × 0.30 × 0.30 mm) crystallized (pentane, –40 °C) in the orthorhombic space group *Pca*2$_1$ (No. 29) with a = 20.674 (2) Å, b = 10.087 (5) Å, c = 19.908 (5) Å, and V = 4151.6 Å^3 with $Z = 4$ (ρ_{calcd} = 1.31 g cm^{-3}) and μ = 27.1 cm^{-1}. Data were collected on a Syntex P2$_1$ diffractometer at 23 ± 1 °C with Mo Kα radiation (λ = 0.71073 Å). A total of 4153 reflections were collected in the h, k, $\pm l$ octants (3799 unique) in the range 2° ≤ 2θ ≤ 50°. Only the 2536 reflections having $I \geq 3\sigma(I)$ were used in the refinements. The structure was solved by direct methods and is at an intermediate stage of refinement (full-matrix least-squares techniques) for a current R = 0.041 and R_w = 0.045. The largest peak in the difference Fourier map has a height of 1.21 e/Å^3. No numerical absorption correction was made, but Lorentz and polarization corrections were applied. The final details will be provided in a full report.

(21) Selected interatomic distances (Å): Ta–O(10) = 1.876 (6), Ta–O(20) = 1.861 (6), Ta–Cl = 2.343 (3), N–C(1) = 1.48 (2), C(1)–C(2) = 1.46 (1), C(2)–C(3) = 1.43 (2), C(3)–C(4) = 1.46 (2), C(4)–C(5) = 1.35 (2), C(5)–N = 1.386 (9). Selected bond angles (deg, (N,C) = N–C(1) midpoint): Ta–O(10)–C(11) = 161.7 (7), Ta–O(20)–C(21) = 165.1 (6), (N,C)–Ta–O(10) = 116.3 (3), (N,C)–Ta–O(20) = 112.2 (2), (N,C)–Ta–Cl = 110.9 (1), O(10)–Ta–O(20) = 117.3 (4), O(10)–Ta–Cl = 95.2 (3), O(20)–Ta–Cl = 102.5 (2), Ta–C(1)–N = 63.1 (6), Ta–N–C(1) = 75.2 (7).

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Novel Allene–Acetylene Cross-Condensation Catalyzed by Palladium Complexes

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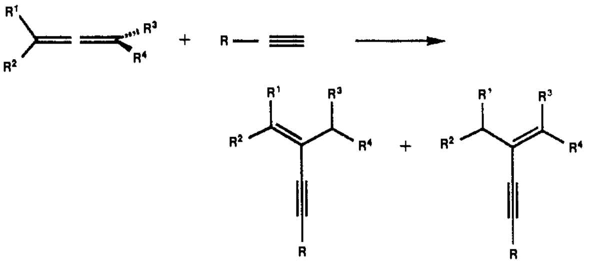
The high propensity for allenes to undergo oligomerization in the presence of Pd catalysts[1] has greatly limited their usefulness as substrates for C–C bond formation with such catalysts.[2] The increasing synthetic availability of allenes enhances their attractiveness as reactive building blocks. In our search for new condensation reactions to maximize synthetic efficiency in which the product is the simple sum of the reactants, we were attracted to the reaction of eq 1. In this paper, we report our preliminary results, in which we succeeded in achieving such a condensation with an unusual dependence of product regioselectivity on the choice of catalyst.[3]



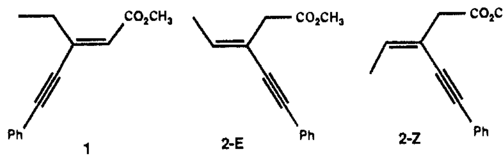
(1)

The sensitivity of the allenes toward oligomerization with palladium complexes was revealed by our earlier failures to effect cycloisomerizations of enallenes, a process that ultimately succeeded with a nickel–chromium catalyst.[4,5] In contrast to that study, exposing an equimolar mixture of phenylethyne and methyl 2,3-pentadienoate to various palladium(2+) catalysts in benzene at 65 °C gave cross-coupled products as summarized in Table I. The most striking feature of this table is the favoring of the conjugated enoate **1** with the more electron deficient catalyst systems (optimized at 81:19 of **1**:**2**) and the favoring of the nonconjugated enoates **2** with the more electron rich catalyst systems (optimized at 9:91 of **1**:**2**).

Table II and eq 2 illustrate the generality with respect to the acetylene and 1,2-disubstituted allenes. In all cases, catalyst A (see Table I entry 1) gave products of type **3**[7] predominantly, but catalyst B (see Table I, entry 5) gave predominantly enynes **4**.[7]

Allene substitution dramatically affects the regioselectivity. 1,1-Di- and 1,1,3-trisubstituted allenes **5** and **6** give the conjugated enoates **7**[7] and **8**[7] regardless of the catalyst. On the other hand,

Table I. Catalyst Dependence of Condensation of Phenylethyne and Methyl 2,3-Pentadienoate



entry	catalyst[a]	**1**, %	**2**-E, %	**2**-Z, %	yield[b,c]
1	4% Pd(OAc)$_2$, TDMPP (cat. A)	76	18	6	55
2	4% Pd(OAc)$_2$, TTMPP	66	29	5	(55)
3	4% Pd(OAc)$_3$, Ph$_3$P	81	19		(43)
4	4% TCPC, TDMPP	42	37	21	(62)
5	4% TCPC, TTMPP (cat. B)	9	47	44	(64)
6	4% TCPC, Ph$_3$P	83	17		(48)
7	4% (CH$_3$CN)$_2$PdCl$_2$, TDMPP	58	21	21	38

[a] TDMPP = tris(2,6-dimethoxyphenyl)phosphine; TTMPP = tris(2,4,6-trimethoxyphenyl)phosphine; TCPC = tetrakis(carbomethoxy)palladacyclopentadiene.[6] [b] Yields either are for isolated product or are determined by NMR spectroscopy (in parentheses). [c] See ref 7.

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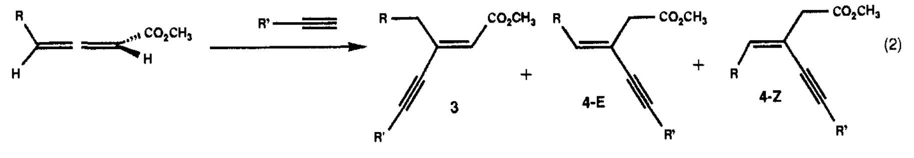
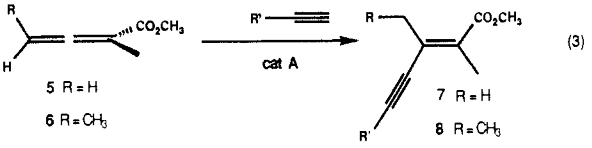
Table II. Cross-Condensation of Methyl 2,3-Alkadienoates with Terminal Acetylenes

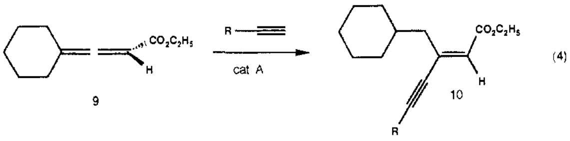


R	R^1	cat.	yield, %	**3**, %	**4**-E, %	**4**-Z, %
CH_3	$CH_3(GH_2)_5$	A	74	85	12	3
		B	53	6	47	47
CH_3	$PhOCH_2$	A	37	87	9	4
		B	51	8	46	46
$C_2H_5OCH_2$	$CH_3(CH_2)_5$	A	66–81	85	13	2
	$PhOCH_2$	A	43	63	33	4
		B	33		11	22
ic_3H_7	TMS	A	39	67	20	13
		B	57	10	65	25

the β,β-disubstituted allene **9** gives the β,γ-enoates **10**[7] regardless of catalyst (eq 4).



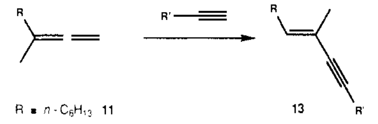
R'	7	8
= $CH_3(CH_2)_5$	74%	60%
= $PMBOCH_2$	73%	--
= $MEMOCH_2$	--	32%
= TMS	83%	66%
= $(CH_3O_2C)_2CHCH_2$	77%	46%



R	
= Ph	64% (cat B 72%)
= TMS	81%
= $MEMOCH_2$	42%

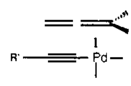
While the presence of an electron-withdrawing group on the allene aids the condensation, it is not obligatory. The monoalkylallenes **11** and **12** cross-condense with terminal acetylenes in somewhat lower yields (eq 5). In complete contrast to allenes bearing an ester substituent, these show no regioselectivity dependence on catalyst.

Several aspects of this new condensation are noteworthy. In spite of the rapid self-condensation of terminal acetylenes, the presence of only stoichiometric amounts of allene can totally redirect the reaction pathway to cross-condensation. The regioselectivity dependence on catalyst is most unusual, A possible explanation may relate to the preferential coordination of an active palladium intermediate to the 2,3-double bond as in **15** with a more electron rich palladium complex (leading to the β,γ-unsaturated ester products) but to the 3,4-double bond as in **16** with a less electron rich palladium complex (leading to the α,β-unsaturated ester products). Steric effects as in the cases of allenes **5**, **6**, and **9** override this electronic bias. Alternatively, relatively nonpolarized allenes as in the case of **11** and **12** simply reflect steric effects.



R'	13	14
Ph	62%	54%
s - C_6H_{13}	30%	48%

(5)



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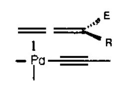
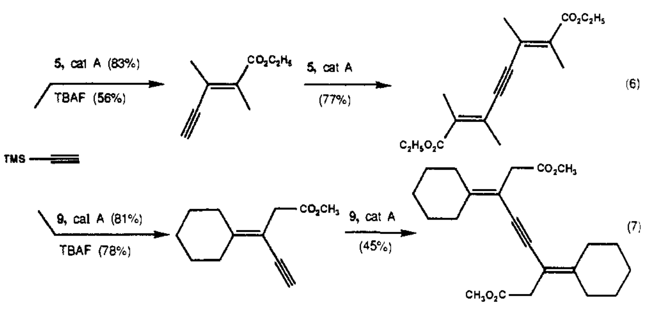
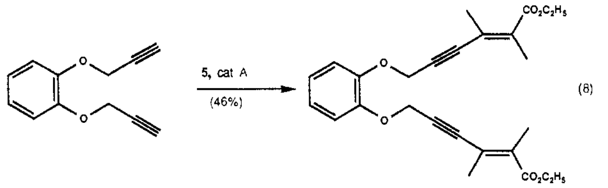
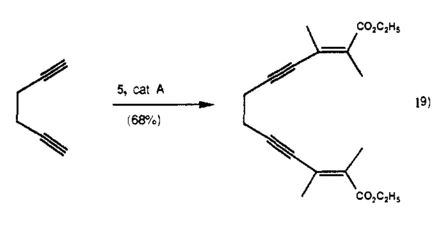


16

This new condensation protocol easily permits access to more highly unsaturated products. For example, (trimethylsilyl)-acetylene can be employed as a linchpin to build 1,5-dien-3-ynes (eqs 6 and 7) Diynes undergo parallel condensations to produce bis(enynes) (eqs 8 and 9). The ability to effect this cross-con-







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(3) The condensation of allene and propyne, using palladium nitrate in acetic acid containing various modifiers, to produce low yields of mixtures of products, one of which is reported to be the result of the cross-condensation, has been recorded. See: Shier, G. D. U.S. Patent 3458562; *Chem. Abstr.* **1969**, *71*, 80641p.

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(7) All new compounds have been fully characterized spectrally, and elemental composition has been established by high-resolution mass spectroscopy or combustion analysis.

densation with allenes provides great flexibility with respect to the substitution of the olefin in the resultant enynes, a feature not available with other condensations.[8] The simplicity and versatility of this method should make it a valuable entry to enynes and dienynes, as well as poly(enynes), useful functional building blocks and substances of growing pharmacological interest. Exploring the mechanism of this cross-condensation also represents an important avenue for future work.[9]

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Supplementary Material Available: Spectroscopic and analytical details for **1**, **2**-E, **3**, **4**-E, **7**, **8**, **10**, **13**, and **14** (5 pages). Ordering information is given on any current masthead page.

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(8) Trost, B. M.; Chan, C.; Ruhter, G. *J. Am. Chem. Soc.* **1987**, *109*, 3486.

(9) In a typical experimental procedure, the terminal acetylene and allene in an approximately 1:1 ratio was added to a solution of 3 mol % of either TCPC or palladium acetate and 3 mol % of the ligand in benzene to create a solution that was approximately 0.2–0.3 M in substrates. After stirring at 50–60 °C until the starting material disappeared, evaporation and chromatographic separation gave the purified products.

On the Anomaly of the Metal–Carbon Bond Strength in $(CH_3)_2M$ Compounds of the Heavy Elements M = Au^-, Hg, Tl^+, and Pb^{2+}. Relativistic Effects in Metal–Ligand Force Constants

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In this paper attention is drawn to the fact that relativistic effects are important in force constants involving heavy metal-ligand bonds. The trend in the metal–carbon bond strength in dimethyl complexes of the Hg, Tl, and Pb follows an unexpected order,[1] Figure 1. The metal–carbon stretching force constants in the isoelectronic series MMe_2 (M = Cd, In^+, and Sn^{2+}; Me = CH_3) increase from the left to the right due to the increasing nuclear charge, i.e., $k_e(CdMe_2) < k_e(InMe_2^+) < k_e(SnMe_2^{2+})$. In contrast, a decrease is observed for the heavy metal series, $k_e(HgMe_2) > k_e(TlMe_2^+) > k_e(PbMe_2^{2+})$.[2,3] The unusually large k_e(M–C) has been discussed in terms of 5d participations in the M–C bond[1,3-8] or due to the possibility of hydration effects on the positively charged species.[2] However, the origin of this anomaly still remains unknown, It has been suggested recently[5] that the unusually large force constant in $HgMe_2$ may be attributed to relativistic effects. Relativistic effects in force constants have not been studied extensively.[9,10] In the series Au, Hg, Tl, and Pb the relativistic 6s-orbital contraction decreases from the left to the right ("Au-maximum"; see ref 9). Hence, we expect the largest relativistic change in molecular properties in $AuMe_2^-$ and the smallest in $PbMe_2^{2+}$. This would explain the anomaly in force constants discussed above. This communication shows that the decrease in M–C force constants from $HgMe_2$ to $TlMe_2^+$ is due to relativistic effects, whereas the decrease from $TlMe_2^+$ to $PbMe_2^{2+}$ is also revealed at the nonrelativistic level.

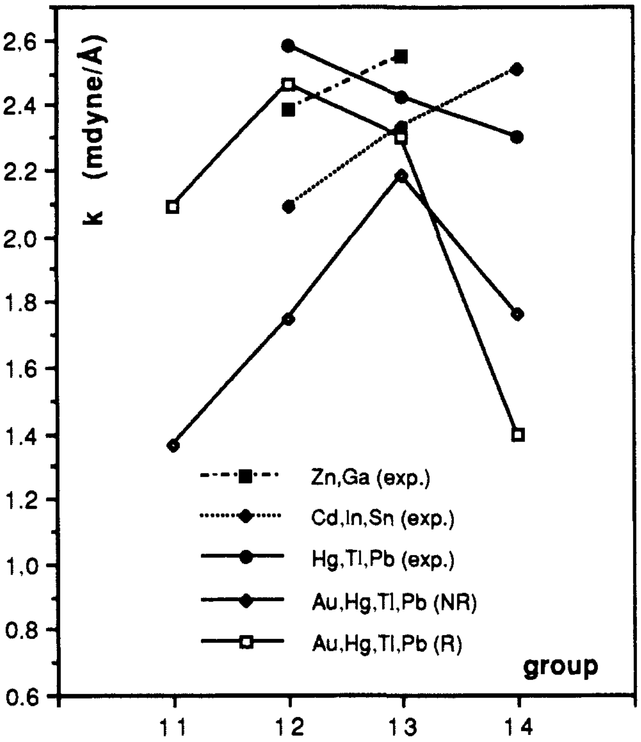

Figure 1. Variation of the metal–carbon stretching force constants in the isoelectronic series $ZnMe_2$, $GaMe_2^+$, $CdMe_2$, $InMe_2^+$, $SnMe_2^{2+}$, $HgMe_2$, $TlMe_2^+$, and $PbMe_2^{2+}$ taken from generalized valence force fields (refs 2, 3, and 20). The experimental force constant for $GaMe_2^+$ has been estimated from ref 2.

To solve this long-standing problem, nonrelativistic (NR) and relativistic (R) Hartree–Fock (HF) calculations using multielectron adjusted spin-orbit averaged pseudopotentials for gold, mercury, thallium, and lead have been performed for $AuMe_2^-$, $HgMe_2$, $TlMe_2^+$, and $PbMe_2^{2+}$.[11] The HF geometries have been optimized.[11,12] The M–C bond distances and symmetric stretching force constants have been derived from a second-order Møller–Plesset perturbation method (MP2)[11,12] The basis sets and pseudopotentials are described in refs 5, 13, 14, and 15.

The MP2 metal–carbon bond lengths and symmetric stretching force constants are in close agreement with the latest experimental results (Table I). The largest relativistic change in r_e(MC) and $k_e(M-CH_3)$ has been calculated for $AuMe_2^-$, Table II. It is evident that relativity is the reason for the anomaly in the metal–carbon bond strength of mercury and thallium; i.e., the nonrelativistic calculated force constants show the expected increase as obtained for the methyl complexes of the elements in the fifth (and possibly of the fourth) period of the periodic table, Figure

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[†] Present address: Research School of Chemistry, The Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601, Australia.

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(12) For $HgMe_2$ a basis set of 169 primitive Gaussians contracted to 109 basis functions has been used. A HF geometry optimization required about 25 h CPU time on a IBM3081 computer. A one-point MP2 (CISC) calculation required about 2 (30) h CPU time.

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