A weak absorption in this region has been reported by Andrews and Ozin for matrix-isolated Cr_2.[8c] Hot bands arising from ($v_{neutral}$ = 0) ← (v_{ion} = n, n = 1–3) transitions to this excited state, shown at ×5 magnification in Figure 1, yield ω_e = 470 ± 25 cm^{-1} and $\omega_e x_e$ = 20 ± 10 cm^{-1} for the Cr_2^- anion.

The ×20 inset to Figure 1 displays an expansion of the spectrum near the ground-state transition. As shown on the right side of the inset, vibrational states of neutral Cr_2 from v = 2 to v = 6 are observed 875, 1275, 1650, 1995, and 2305 cm^{-1} (±15 cm^{-1}) above the 0–0 transition. These features are far more intense than would be expected on the basis of Franck-Condon factors for a direct photodetachment process. With the v = 1 level constrained to its literature value,[6] the observed energies can be fit to within our experimental uncertainty to a Morse potential with ω_e = 479 ± 2 cm^{-1} and $\omega_e x_e$ = 13.5 ± 1.0 cm^{-1}. This anharmonicity constant is unusually large: $\omega_e x_e$ values for all other neutral homonuclear first-row transition-metal dimers measured to date[3] fall in the range 1–4 cm^{-1}. Interestingly, the excellent Morse potential fit to vibrational levels up to v = 6 (0.3 eV above the zero-point level) extrapolates to a dissociation asymptote of only 0.5 eV, far below the true[4] Cr_2 bond energy (D_o) of 1.44 ± 0.05 eV. Thus, it is clear that the Cr_2 ground-state potential energy curve strongly diverges from a Morse potential at higher energies.

A weak vibrational progression of the neutral molecule comprising more than a dozen peaks is observed from 5100 to 6700 cm^{-1} above the 0–0 transition, as shown on the left side of the ×20 inset to Figure 1. Surprisingly, the peak spacings are only 130 ± 10 cm^{-1}, and they exhibit no detectable anharmonicity. This low-frequency, harmonic vibrational progression displays an intensity profile noticeably more irregular than that expected for the photoelectron spectrum of a diatomic species. Furthermore, the intensity profile changes dramatically when the argon ion laser is tuned from 488 nm to any of the other lines (476, 496, or 514 nm) strong enough to be used in this experiment. The relative intensities of the v = 2 to v = 6 features discussed above also exhibit a pronounced wavelength dependence. In all cases, however, the separation between each peak and the 0–0 transition does not vary with laser wavelength. These observations suggest a one-photon process involving a resonance of the laser with one or more metastable states of the negative ion. The analogous formation of intermediate autoionizing resonances is well-documented in the literature of neutral molecule photoelectron spectroscopy.[19,20] This propitious resonance allows us to probe regions of the neutral molecule potential curve that would normally be inaccessible in this experiment due to negligible Franck–Condon overlap with the anion ground state.

The 130-cm^{-1} vibrational interval observed here is close to the 110-cm^{-1} value predicted by Goodgame and Goddard[10] for the singly 4s–4s bonded, "long-bond form" of the Cr_2 ground state. However, the 130-cm^{-1} progression appears only 0.6 eV above the 0–0 transition and displays no detectable anharmonicity over a 0.2-eV range. In contrast, the MGVB calculation[11] predicts the 4s–4s well to be bound by only 0.3 eV and to lie 1.6 eV above the 3d–3d well. No long-bond excited electronic states are predicted at lower energies. In addition, we measure an unusually large anharmonicity ($\omega_e x_e$ = 13.5 ± 1.0 cm^{-1}) for the "short-bond" region of the potential. These results suggest the need for improved calculations of the ground-state potential energy curve of Cr_2.

# Synthesis of Indoles via Palladium-Catalyzed Heteroannulation of Internal Alkynes

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The indole nucleus is prevalent in a wide variety of biologically active, naturally occurring compounds, and numerous approaches to its synthesis have been reported, including many employing transition metals,[1] particularly palladium.[2] Our interest in the palladium-catalyzed annulation of 1,2-dienes,[3] 1,3-dienes,[4] and unsaturated cyclopropanes and cyclobutanes[5] encouraged us to examine analogous alkyne chemistry for the synthesis of indoles.

There has been considerable interest of late in transition-metal-mediated cycloaddition reactions of alkynes in organic synthesis,[6] especially those involving palladium.[7] With a few exceptions, intermolecular attempts to annulate onto alkynes using palladium have generally resulted in multiple alkyne insertions or in insertion and subsequent cyclization back on to a preexisting aromatic ring (eq 1).[8]

1
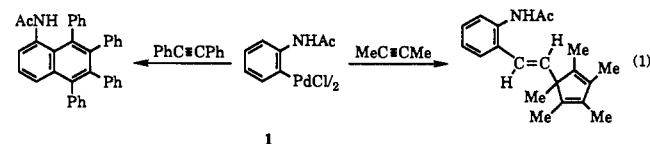
We now report a conceptually and experimentally simple, new approach to indoles involving the palladium-catalyzed heteroannulation of internal alkynes using *o*-iodoaniline and its derivatives (eq 2).[9] Our results are summarized in Table I.
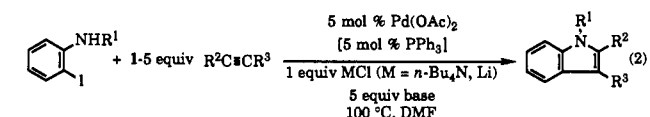
In general, we have used a procedure similar to those used by us for earlier annulation processes. Carbonate or acetate bases, in the presence or absence of catalytic amounts of triphenylphosphine, have afforded the best results. All of our early work was carried out by using 1 equiv of *n*-Bu$_4$NCl (Lancaster, pro-

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Table I. Synthesis of Indoles via Palladium-Catalyzed Annulation of Alkynes (Eq 2)^a

entry	R^1	R^2	R^3	alkyne equiv	procedure	base	PPh$_3$	time, h	% isolated yield^b
1	H	n-Pr	n-Pr	5	A	K$_2$CO$_3$	+	16	70
2				5	B	K$_2$CO$_3$	–	24	80
3				2	B	K$_2$CO$_3$	–	24	64
4				1	B	K$_2$CO$_3$	–	24	50
5	Me			5	A	K$_2$CO$_3$	+	24	71
6	Ac			5	A	KOAc	–	24	91
7	Ts			5	A	KOAc	–	24	86
8	H	t-Bu	Me	5	A	Na$_2$CO$_3$	+	24	82
9		c-C$_6$H$_{11}$	Me	5	A	K$_2$CO$_3$	+	16	57
10		1-OH-c-C$_6$H$_{10}$	Et	2	A	Na$_2$CO$_3$	+	24	78
11				2	B	K$_2$CO$_3$	+	24	85
12				1	B	K$_2$CO$_3$	+	24	51
13		CMe$_2$OH	H$_2$C=CMe	2	A	KOAc	–	24	70
14				2	B	KOAc	–	12	67
15		Me$_3$Si	Me	5	A	Na$_2$CO$_3$	+	12	98
16		Me$_3$Si	CH$_2$OH	2	A	Na$_2$CO$_3$	+	24	60
17	Ac	Ph	Me	2	B	KOAc	–	16	75
18				1	B	KOAc	–	16	70
19		CH$_2$OH	Me	2	B	KOAc	–	16	60^c
20	Ts	Ph	Ph	2	B	K$_2$CO$_3$	–	48	60

^{a} All reactions were run by heating to 100 °C 5 mol % Pd(OAc)$_2$, aryl iodide (0.5 mmol), n-Bu$_4$NCl (0.5 mmol, procedure A) or LiCl (0.5 mmol, procedure B), base (2.5 mmol), alkyne (0.5, 1.0, or 2.5 mmol), DMF (10 mL), and where appropriate, 5 mol % PPh$_3$. ^{b} All products gave appropriate ^{1}H and ^{13}C NMR, IR, and mass spectral or elemental analytical data. ^{c} The product is 2-(acetoxymethyl)-3-methylindole.
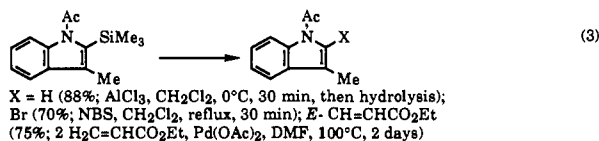
cedure A), but it was subsequently observed that LiCl (procedure B) was often more effective and reproducible. The number of equivalents of LiCl is critical. More than 1 equiv of LiCl sharply lowers the yield and appears to favor multiple insertion products.

This reaction is remarkably versatile as far as the aniline moiety is concerned. The nitrogen may be unsubstituted or bear groups as diverse as a methyl, acetyl, or tosyl group. Bromoanilines are generally unreactive, however.

A wide variety of internal alkynes have been successfully employed in this process. The more volatile the alkyne is, the greater the amount of alkyne that has been employed, although good yields can still be obtained by using lesser amounts (compare entries 2–4). The alkyne can bear alkyl, aryl, alkenyl, hydroxy, and silyl groups. Even bulky tertiary alkyl or trimethylsilyl groups are readily accommodated and indeed tend to afford the highest yields.

The annulation of unsymmetrical alkynes has proven to be highly regioselective, providing only the regioisomer shown in Table I. The more sterically bulky group ends up nearer the nitrogen atom in the indole product. This selectivity is consistent with previous work on the palladium-catalyzed hydroarylation of internal alkynes, although our reactions appear to be significantly more regioselective.[10] Even 1-phenyl-1-propyne (entries 17 and 18) and 1-cyclohexylpropyne (entry 9) afford only one regioisomer. Surprising regioselectivity is even observed in the reaction of o-iodoaniline and 2-pentyne, which produces a 2:1 mixture of regioisomers. Indeed, excellent regio- and chemoselectivity is observed with alkynes as diverse as 2-butyn-1-ol (entry 19) and 2,5-dimethyl-5-hexen-3-yn-2-ol (entries 13 and 14).

The facile annulation of silylalkynes broadens tremendously the scope of this synthetic process. Desilylation by acylation,[11] protonolysis, halogenation, or the Heck reaction provides a convenient entry into variously substituted indoles (eq 3).

X = H (88%; AlCl$_3$, CH$_2$Cl$_2$, 0°C, 30 min, then hydrolysis);
Br (70%; NBS, CH$_2$Cl$_2$, reflux, 30 min); E- CH=CHCO$_2$Et
(75%; 2 H$_2$C=CHCO$_2$Et, Pd(OAc)$_2$, DMF, 100°C, 2 days)

This indole synthesis presumably proceeds via (1) oxidative addition of the aryl iodide to Pd(0), (2) syn insertion of the alkyne into the arylpalladium bond, and (3) nitrogen displacement of the palladium in the resulting vinylpalladium intermediate, quite

possibly by halide displacement to form a six-membered-ring, heteroatom-containing palladacycle and subsequent reductive elimination. Although there are previous examples of this last step,[7] the dramatic difference in our results and those reported earlier using a virtually identical complex 1 (eq 1)[8] is remarkable.

Supplementary Material Available: Description of procedures for annulation and all reactions described in eq 3 and experimental data, including IR, ^{1}H and ^{13}C NMR, and exact mass spectra and elemental analyses, for all products (6 pages). Ordering information is given on any current masthead page.

New Methodology for the Synthesis of Functionalized Indolizidine and Quinolizidine Ring Systems

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The widespread occurrence of indolizidine and quinolizidine systems across many families of alkaloids[1] warrants the further development of new and more efficient synthetic methodologies that can be targeted toward those members that reveal promising biological profiles.[2] We report a new strategy for the construction of these structural subunits. Our general scheme involves the reaction of 2-vinylazacycles 1 with the appropriate ketene, which generates zwitterionic intermediates 2 that undergo facile [3, 3] ring expansions[3] to give macrocyclic lactams 3 (eq 1).[4] This mode

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