of these is a semibridge across the Ru(1)-Ru(3) bond, Ru(3)···C(13) = 2.420 (8) Å. Compound 3 contains 94 valence electrons. According to the PSEP theory, a capped pentagonal bipyramidal cluster containing two main-group elements should contain 92 electrons; thus **3**, like **2**, is electron-rich by two electrons, and this may account for the weakening and lengthening of the two metal-metal bonds Ru(1)-Ru(6) and Ru(3)-Ru(4). The transformation of **2** to **3** involves the loss of only one carbonyl ligand, but there has been a considerable rearrangement of the metal-metal and metal-sulfur bonding and a repositioning of the ynamine ligands. At this time, we cannot predict the course of this transformation.

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Supplementary Material Available: Tables of bond angles, anisotropic thermal parameters, and positional parameters of the hydrogen atoms for all three crystal analyses (17 pages); listings of structure factor amplitudes for **2** and **3** (43 pages). Ordering information is given on any current masthead page.

Biphasic and Phase Transfer Catalyzed N-Monoacylation and N,N′-Diacylation of Azobenzenes by Cobalt Carbonyl

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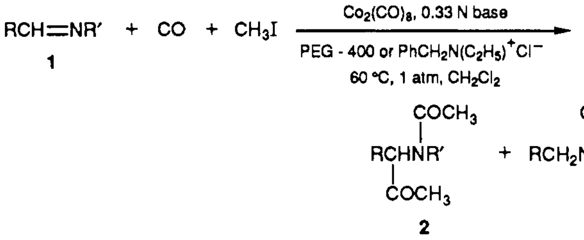
Azobenzenes react with a stoichiometric amount of cobalt carbonyl and excess methyl iodide under phase-transfer conditions (benzene, water, and benzyltriethylammonium chloride as the phase-transfer agent) to give acetic acid 1,2-diaryl-2-acetylhydrazides in reasonable yields. Byproducts arising from nitrogen-nitrogen bond cleavage were formed in several of the reactions. Reductive monoacylation of azobenzenes occurs on reaction with $Co_2(CO)_8$, methyl iodide, and a catalytic amount of *p*-toluenesulfonic acid under biphasic conditions.

One of the most useful organometallic phase-transfer-catalyzed processes is that which involves the in situ generation of acylcobalt tetracarbonyl[1] by treatment of cobalt carbonyl with carbon monoxide and methyl iodide in an organic-aqueous biphasic system containing a phase-transfer agent.[2,3] Examples include the conversion of alkynes to lactones[4] and the acylation of conjugated dienes[5] as well as azadienes.[6] Recently, the diacylation of Schiff bases (i.e., **1** → **2**) was observed with reductive monoacylation (**3**) occurring, to some extent, in most cases.[7]



Most of the chemistry of azobenzenes with metal carbonyls has involved the formation of either ortho-metalated complexes[8] or π-complexes.[9] Heterocyclic compounds such as 2-phenylindazolones have been synthesized by carbonylation of several of the ortho-metalated complexes. We now report that azobenzenes undergo diacylation or monoacylation with cobalt carbonyl and methyl iodide, under phase-transfer or biphasic conditions.

Table I. Phase-Transfer-Catalyzed N,N′-Diacylation of Azobenzenes[a]

Ar_1, Ar_2 for 4	amt of 5, %	amt of 6/7, %	amt of recovered 4, %
Ph	54[b]	0	16
p-$CH_3C_6H_4$	52	0	23
m-$CH_3C_6H_4$	52	0	28
p-ClC_6H_4	36	0	38
Ph, *p*-$CH_3OC(O)C_6H_4$	53	0	28
Ph, *p*-HOC_6H_4	28[d]	17	14[c]
Ph, *p*-$CH_3OC_6H_4$	18	13	38
p-$CH_3OC_6H_4$	14	21	20
$C_5H_{10}NC(O)$	0[e]	0	0

[a] Reaction conditions: **4** (2.0 mmol), $Co_2(CO)_8$ (4.0 mmol), CH_3I (62 mmol), $PhCH_2N(C_2H_5)_3^+Cl^-$ (0.5 mmol), C_6H_6 (24 mL), H_2O (24 mL), 60 °C, overnight, N_2 atmosphere. Yields of all products, and recovered **4**, are for pure materials. Crude yields were higher. [b] 1% of $PhNHN(Ph)COCH_3$ was also formed in the reaction. [c] 23% of $PhN{=}NC_6H_4OCOCH_3$-*p* was also isolated. [d] Consisted of 19% **5** (Ar_1 = Ph, Ar_2 = *p*-$CH_3COOC_6H_4$) and 9% **5** (Ar_1 = Ph, Ar_2 = *p*-HOC_6H_4). [e] 93% of $C_5H_{10}NCONHN(CONC_5H_{10})COCH_3$.

Results and Discussion

Treatment of azobenzene (**4**, $Ar_1 = Ar_2$ = Ph) with cobalt carbonyl and methyl iodide in benzene and water containing benzyltriethylammonium chloride as the phase-transfer agent, overnight at 60 °C (nitrogen atmosphere), afforded acetic acid 1,2-diphenyl-2-acetylhydrazide (**5**, $Ar_1 = Ar_2$ = Ph) in 54% isolated yield. A 2/1 ratio of $Co_2(CO)_8$/azobenzene was used in these reactions (use of a 1/1 and 1/2 ratios of $Co_2(CO)_8$/azobenzene gave **5** in 18% and 5% yields, respectively). The best ratio of **4**/benzyltriethylammonium chloride was 4/1. The reaction is applicable to other azo compounds, and the results are presented in Table I. Reasonable yields of pure acetic acid

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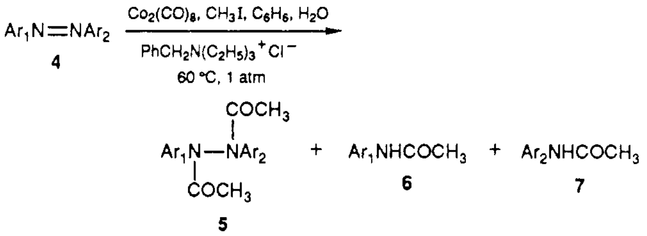
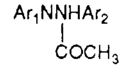


1,2-diaryl-2-acetylhydrazides (**5**) were obtained from azobenzenes containing methyl, chloro, and acetoxy substituents. However, the presence of hydroxy or methoxy functionalities results in appreciable nitrogen–nitrogen bond cleavage to give amides **6** and **7** as well as **5**. Surprisingly, 1,1′-(azodicarbonyl)dipiperidine was converted in 93% yield to the acetic acid hydrazide **8** ($Ar_1 = Ar_2 = C_5H_{10}NC(O)$).


$$Ar_1N(COCH_3)NHAr_2$$

8

The diacylation process is stoichiometric with respect to the metal carbonyl, in contrast to the results obtained with use of Schiff bases.[7] The phase-transfer agent is essential for the reaction, as only traces of $PhNHN(Ph)COCH_3$ and PhNHNHPh were obtained when the reaction of azobenzene was effected in the absence of a quaternary ammonium salt. Hydrazobenzene was formed in 15% yield (83% recovered azo compound) when azobenzene was reacted in the absence of methyl iodide. Methylene chloride can be used as the organic phase (instead of benzene), but the yield of **5** is appreciably less (e.g., 20% in the case of **5**, $Ar_1 = Ar_2 = Ph$). Replacement of water by 0.5 M sodium hydroxide as the aqueous phase also resulted in lower conversions of azo compounds. Finally, similar results were obtained by use of either a nitrogen or carbon monoxide atmosphere in these reactions.

An infrared spectrum recorded 30 min after the addition of methyl iodide to a mixture of cobalt carbonyl, benzyltriethylammonium chloride, water, and benzene under carbon monoxide at 30 °C (i.e. without azobenzene) showed carbonyl stretching bands in the infrared region at 2110 (w), 2050 (s), 2020 (s), and 1710 (m) cm^{-1} consistent with the presence of $CH_3COCo(CO)_4$[10] but different from $CH_3COCo(CO)_3I^-$.[11]

A possible mechanism for the conversion of azoarenes to **5** is outlined in Scheme I (illustrated for azobenzene). Acetylcobalt tetracarbonyl (**9**), generated from cobalt carbonyl, carbon monoxide, and methyl iodide, reacts with the azo substrate to give **10**. Reaction of the latter with additional **9** could give the product and regenerate dicobalt octacarbonyl. However, in contrast to the case of Schiff bases, this step is unlikely as the azobenzene reactions are stoichiometric rather than catalytic in nature.

Alternatively, reaction of **10** with $HCo(CO)_4$ (generated from $Co(CO)_4^-$ and H_2O) can give the acetic acid hydrazide (**11**, an analogue of **8**) and dicobalt octacarbonyl. The hydrazide can react with more of **9** to form **12**, which is then convertible to **5**. Support for this pathway comes from the reaction of **11** with $Co_2(CO)_8$ and methyl iodide under phase-transfer conditions identical with those employed for azobenzene. In this case, **11** afforded acetic acid 1,2-diphenyl-2-acetylhydrazide (**5**) in quantitative yield.

Scheme I

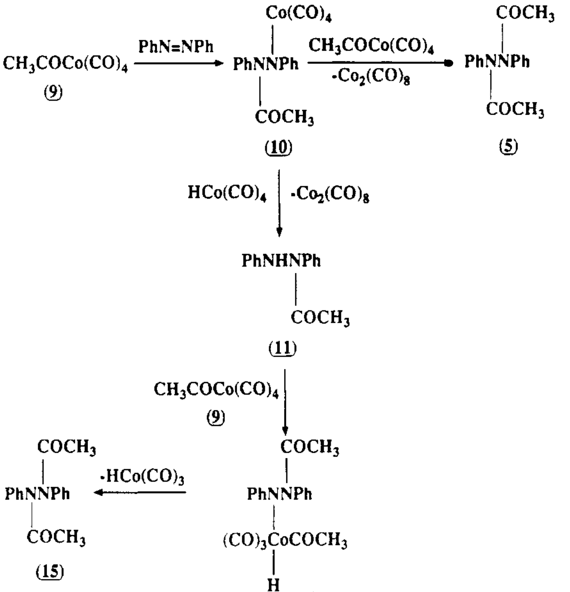


Table II. N-Monoacylation of Azo Compounds by $Co_2(CO)_8$ and p-TsOH[a]

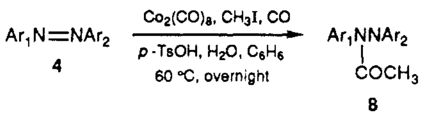
Ar_1, Ar_2 for **4**	amt of p-TsOH, equiv	amt of products,[b] %			amt of recovered **4**, %
		8	**5**	hydrazine deriv	
Ph	0.02	48	0	trace	39
p-$CH_3C_6H_4$	0.02	13	11	trace	54
	0.06	29	6	0	50
m-$CH_3C_6H_4$	0.02	14	4	18	41
	0.10	28	0	5	48
p-ClC_6H_4	0.02	37	0	8	39
$C_5H_{10}NC(O)$	0.02	80	0	0	0

[a] Reaction conditions: **4** (2.0 mmol), $Co_2(CO)_8$ (2.0 mmol), CH_3I (62 mmol), C_6H_6 (24 mL), H_2O (24 mL), CO (1 atm), 60 °C, overnight. [b] Yields are of pure materials.

The azobenzene reaction does not proceed via initial reduction to hydrazobenzene followed by stepwise acylation, since use of hydrazobenzene as the reactant gave **5** ($Ar_1 = Ar_2 = Ph$) in only 4% yield and 8% of **8** ($Ar_1 = Ar_2 = Ph$), with the remainder being recovered hydrazobenzene.

The occurrence of some nitrogen–nitrogen bond cleavage when 4-hydroxy-, 4-methoxy, and 4,4′-dimethoxyazobenzene were used as reactants may be due to participation of lone-pair electrons of the oxygen atom of the substituent group in an intermediate such as **14** (analogue of **10**) (Scheme II).

Having found a process to directly diacylate azoarenes, a study was undertaken to develop a selective method for reductive monoacylation. The best results were obtained by using acidic conditions. Treatment of an azo compound with a stoichiometric quantity of cobalt carbonyl, excess methyl iodide, carbon monoxide, and a catalytic amount of p-toluenesulfonic acid (p-TsOH) in benzene and water, overnight at 60 °C, afforded the acetic acid hydrazide (**8**) as the main product in fair to good yields (see Table II for results).



The millimolar ratio of $4/Co_2(CO)_8/p$-TsOH used was 2/2/(0.02–0.10). With use of 0.02 equiv of p-TsOH, the acylation of azobenzene and 1,1′-(azodicarbonyl)di-

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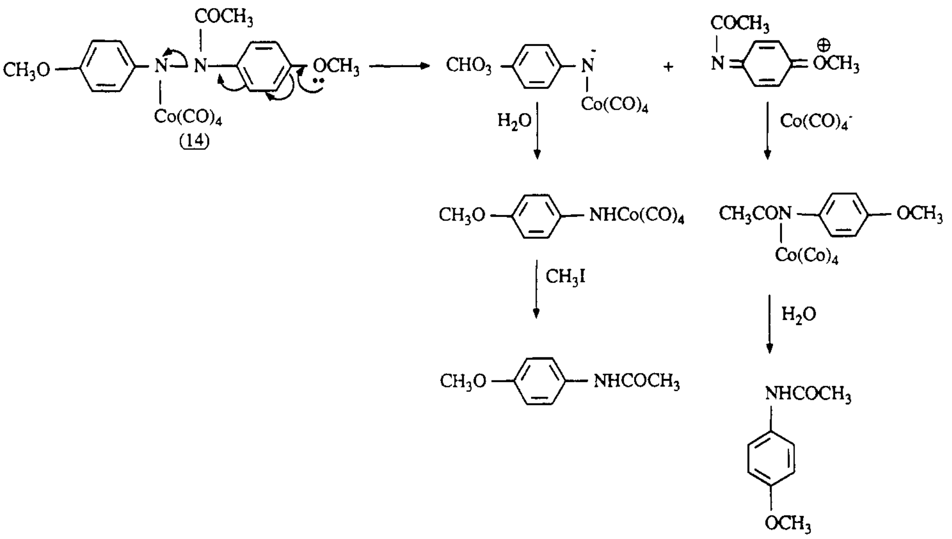
Scheme II



piperidine was highly selective, affording 48% and 80%, respectively, of the acetic acid hydrazide. More *p*-TsOH was needed in order to obtain fair yields of monoacylated products from 3,3′- and 4,4′-dimethylazobenzene. Low conversion and selectivity in the reaction of azobenzene results with use of a stoichiometric amount of *p*-TsOH. Also, increasing the quantity of cobalt carbonyl resulted in lower selectivity (e.g., 2/1 $Co_2(CO)_8$/azobenzene gave 8, $Ar_1 = Ar_2 = Ph$, in 29% yield).

It is conceivable that hydridotetracarbonylcobalt, $HCo(CO)_4$, may be generated under the acidic reaction conditions, and addition to the azo moiety would give $Ar_1NHN(Ar_2)Co(CO)_4$. Reaction of the latter with methyl iodide and carbon monoxide may lead to $Ar_1NHN(Ar_2)$-$Co(CO)_3COCH_3$, which on reductive elimination in the presence of carbon monoxide can give 8 and $ICo(CO)_4$.[12]

In conclusion, azobenzene can be converted to N-monoacylated or N,N′-diacylated products by cobalt carbonyl, depending on the reaction conditions.

Experimental Section

General Considerations. Melting point determinations were made on a Fisher-Johns apparatus and are corrected. Elemental analyses were carried out by either Guelph Chemical Laboratories, Guelph, Ontario, Canada, or MHW Laboratories, Phoenix, AZ. Infrared spectral determinations were made with a Perkin-Elmer 783 spectrometer. A VG7070E spectrometer was used for mass spectral determinations, while nuclear magnetic resonance spectra were recorded on Varian XL-300 or EM-360 spectrometers.

Azo Compounds. Azobenzene, 4-hydroxyazobenzene, and 1,1′-(azodicarbonyl)dipiperidine were purchased from Aldrich Chemical Co. and were recrystallized prior to use. The azoarenes $RC_6H_4N{=}NC_6H_4R$, where R = *p*-Cl, *p*-CH_3O, *p*-CH_3, and *m*-CH_3, were prepared in 40–49% yields by following a literature procedure, with hexane used as a solvent for recrystallization in all cases.[13] Compound 4 (Ar_1 = Ph, Ar_2 = *p*-$CH_3OCOC_6H_4$) was prepared in 93% yield by reaction of 4-phenylazophenol with acetyl chloride in the presence of pyridine.[14] 4-Methoxyazobenzene was formed in 90% yield by a phase-transfer-catalyzed reaction of 4-hydroxyazobenzene with methyl iodide.[15]

General Procedure for the Phase-Transfer-Catalyzed Diacylation of Azobenzene with $Co_2(CO)_8$ and Methyl Iodide. A mixture of water (24 mL) and benzene (24 mL) was degassed by bubbling nitrogen through the stirred medium at 60 °C for 30 min. Cobalt carbonyl (1.3 g, 4.0 mmol) was added, followed, at 5-min intervals, by $PhCH_2N(C_2H_5)_3{}^+Cl^-$ (0.114 g, 0.050 mmol), methyl iodide (3.0 mL, 62 mmol), and the azo compound (2.0 mmol). The reaction mixture was stirred overnight at 60 °C (N_2 atmosphere). The two layers were separated, the aqueous phase was extracted with chloroform (24 mL), and the chloroform extract was combined with the benzene phase. The combined organic phase was dried over $MgSO_4$ and concentrated by rotary evaporation. The crude products were purified by silica gel chromatography (thin layer or column) with use of appropriate mixtures of hexane/ethyl acetate. Either 7/3 or 1/1 mixtures of hexane/ethyl acetate were used in the case of thin-layer chromatography, while a 9.5/0.5 solvent ratio was initially used for column chromatography followed by a gradual increase in the proportion of ethyl acetate. Further purification, if required, was effected by recrystallization from ether.

Data for 5. 5 ($Ar_1 = Ar_2$ = Ph): IR (ν_{CO}) 1700, 1677 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.96 (s, 6 H, CH_3), 7.29 (s, 10 H, 2 Ph); ^{13}C NMR ($CDCl_3$) δ 22.32 (CH_3), 128.17, 128.88, 129.48, 141.27 (aromatic carbons), 168.32 (carbonyl); MS (*m/e*) 268 [M]$^+$; 226 [M − CH_2CO]$^+$, 183 [M − CH_2CO − $COCH_3$]$^+$; mp 106–107 °C (lit.[16] mp 105 °C). Anal. Calcd for $C_{16}N_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.63;, H, 5.76; N, 10.40.

5 ($Ar_1 = Ar_2$ = *p*-$CH_3C_6H_4$): IR (ν_{CO}) 1695, 1673 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.92 (s, 6 H, $COCH_3$), 2.32 (s, 6 H, $CH_3C_6H_4$), 7.09 (s [br], 8 H, aromatic protons); MS (*m/e*) 296 [M]$^+$, 254 [M − CH_2CO]$^+$, 211 [M − CH_2CO − $COCH_3$]$^+$; mp 126–128 °C. Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 73.24; H, 6.52; N, 9.61.

5 ($Ar_1 = Ar_2$ = *m*-$CH_3C_6H_4$): IR (ν_{CO}) 1697, 1673 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.93 (s, 6 H, $COCH_3$), 2.29 (s, 6 H, $CH_3C_6H_4$), 6.83–7.33 (m, 8 H, aromatic protons); MS (*m/e*) 296 [M]$^+$, 254 [M − $COCH_2$]$^+$; mp 110–111 °C. Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 73.13; H, 7.18; N, 9.71.

5 ($Ar_1 = Ar_2$ = *p*-ClC_6H_4): IR (ν_{CO}) 1700, 1672 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.93 (s, 6 H, CH_3), 7.20 (s [br], 8 H, aromatic protons); MS (*m/e*) 340, 338, 336 [M]$^+$; mp 119–121 °C. Anal. Calcd for $C_{16}H_{14}Cl_2N_2O_2$: C, 56.99; H, 4.18; N, 8.31. Found: C, 57.04; H, 4.37; N, 8.42.

5 (Ar_1 = Ph, Ar_2 = *p*-$CH_3COOC_6H_4$): IR (ν_{CO}) 1755 (ester), 1700, 1675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.93 (s, 6 H, $COCH_3$), 2.26 (s, 3 H, CH_3COO), 6.93–7.46 (m, 9 H, aromatic protons); MS (*m/e*) 326 [M]$^+$, 284 [M − CH_2CO]$^+$. Anal. Calcd for $C_{18}H_{18}N_2O_4$: C, 66.24; H, 5.56; N, 8.58. Found: C, 66.00; H, 5.75; N, 8.91.

5 (Ar_1 = Ph, Ar_2 = *p*-HOC_6H_4): IR (ν_{CO}) 1694, 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.93 (s, 6 H, $COCH_3$), 6.60–7.38 (m, 10 H, aromatic and hydroxy protons); MS (*m/e*) 284 [M]$^+$, 242 [M −

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[16] Latosh, N. I.; Pushkareva, Z. V. *Dokl. Akad. Nauk SSSR* **1958**, *124*, 98.

$CH_2CO]^+$. Anal. Calcd for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.43; H, 6.11; N, 9.91.

5 (Ar_1 = Ph, Ar_2 = *p*-$CH_3OC_6H_4$): IR (ν_{CO}) 1695, 1678 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.90 (s, 6 H, $COCH_3$), 3.73 (s, 3 H, OCH_3), 6.56–7.27 (m, 9 H, aromatic protons); MS (*m/e*) 298 $[M]^+$, 256 $[M - COCH_2]^+$. Anal. Calcd for $C_{17}H_{18}N_2O_3$: C, 68.44; H, 6.08, N, 9.39. Found: C, 68.50; H, 5.77, N, 9.23.

5 (Ar_1 = Ar_2 = *p*-$CH_3OC_6H_4$): IR (ν_{CO}) 1694, 1673 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.88 (s, 6 H, $COCH_3$), 3.70 (s, 6 H, OCH_3), 6.63–6.90 (m, 8 H, aromatic protons); MS (*m/e*) 164 $[M]^+$, 122 $[M - COCH_2]^+$; mp 120–122 °C. Anal. Calcd for $C_{18}H_{20}N_2O_4$: C, 65.84; H, 6.14; N, 8.53. Found: C, 65.74; H, 6.01; N, 8.83.

General Procedure for the Acylation of Azoarenes by $Co_2(CO)_8$ and *p*-TsOH. A mixture of distilled water (24 mL), benzene (24 mL), and *p*-TsOH (see Table II for amount) was degassed at 60 °C with use of nitrogen. The gas was changed to carbon monoxide and $Co_2(CO)_8$ (0.68 g, 2.0 mmol) and methyl iodide (3.0 mL, 62 mmol) were added, followed 30 min later by 2.0 mmol of the azo compound. The reaction mixture was stirred overnight at 60 °C under carbon monoxide. The cooled mixture was filtered, the layers were separated, and the aqueous phase was neutralized and extracted with an equal volume of chloroform. The combined organic phase was dried ($MgSO_4$) and concentrated. Purification of the resulting crude product was effected by silica gel chromatography with 7/3 or 1/1 hexane/ethyl acetate as the eluant.

Data for 8. **8 (Ar_1 = Ar_2 = Ph)**: IR (ν_{CO}) 1673 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.22 (s, 3 H, CH_3), 6.55–7.69 (m, 11 H, aromatic protons and NH); MS (*m/e*) 226 $[M]^+$, 183 $[M - COCH_3)^+$; mp 132–133 °C. Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.27; H, 6.30; N, 12.72.

8 (Ar_1 = Ar_2 = *p*-$CH_3C_6H_4$): IR (ν_{CO}) 1672 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.23 (s, 3 H, $COCH_3$), 2.26 (s, 6 H, *p*-$CH_3C_6H_4$), 6.53–7.26 (m, 9 H, aromatic and amino protons); MS (*m/e*) 254 $[M]^+$, 211 $[M - COCH_3]^+$; mp 141–142 °C. Anal. Calcd for $C_{16}H_{18}N_2O$: C, 75.56; H, 7.13; N, 11.01. Found: C, 75.21; H, 7.33; N, 10.63.

8 (Ar_1 = Ar_2 = *m*-$CH_3C_6H_4$): IR (ν_{CO}) 1672 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.22 (s, 3 H, $COCH_3$), 2.26 (s, 6 H, *m*-$CH_3C_6H_4$), 6.56–7.30 (m, 9 H, aromatic and amino protons); MS (*m/e*) 254 $[M]^+$, 211 $[M - COCH_3]^+$; mp 129–130 °C. Anal. Calcd for $C_{16}H_{18}N_2O$: C, 75.56; H, 7.13; N, 11.01. Found: C, 75.93; H, 7.12; N, 11.09.

8 (Ar_1 = Ar_2 = *p*-ClC_6H_4): IR (ν_{CO}) 1678 cm^{-1}; ^1H NMR ($CDCl_3$) 2.16 (s, 3 H, $COCH_3$), 6.50–7.33 (m, 9 H, aromatic and amino protons); MS (*m/e*) 298, 296, 294 $[M]^+$; mp 94–96 °C.

8 (Ar_1 = Ar_2 = $C_5H_{10}NCO$): IR (ν_{CO}) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36–1.83 (m, 12 H, $C(CH_2)_3C$), 2.09 (s, 3 H, $COCH_3$), 3.38 (m, 8 H, CH_2NCH_2), 8.33 (s, 1 H, NH); MS (*m/e*) 296 $[M]^+$; mp 153–154 °C. Anal. Calcd for $C_{14}H_{24}N_4O_3$: C, 56.71; H, 8.17; N, 18.91. Found: C, 56.93; H, 8.10; N, 18.65.

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Registry No. 4 (Ar_1 = Ar_2 = Ph), 103-33-3; 4 (Ar_1 = Ar_2 = *p*-MeC_6H_4), 501-60-0; 4 (Ar_1 = Ar_2 = *m*-MeC_6H_4), 588-04-5; 4 (Ar_1 = Ar_2 = *p*-ClC_6H_4), 1602-00-2; 4 (Ar_1 = Ph, Ar_2 = *p*-$MeOC(O)C_6H_4$), 2918-88-9; 4 (Ar_1 = Ph, Ar_2 = *p*-HOC_6H_4), 1689-82-3; 4 (Ar_1 = Ph, Ar_2 = *p*-$MeOC_6H_4$), 2396-60-3; 4 (Ar_1 = Ar_2 = *p*-$MeOC_6H_4$), 501-58-6; 4 (Ar_1 = Ar_2 = $C_5H_{10}NC(O)$), 10465-81-3; 4 (Ar_1 = Ph, Ar_2 = *p*-$AcOC_6H_4$), 13102-31-3; 5 (Ar_1 = Ar_2 = Ph), 6049-42-9; 5 (Ar_1 = Ar_2 = *p*-MeC_6H_4), 125879-54-1; 5 (Ar_1 = Ar_2 = *m*-MeC_6H_4), 125879-55-2; 5 (Ar_1 = Ar_2 = *p*-ClC_6H_4), 125879-56-3; 5 (Ar_1 = Ph, Ar_2 = *p*-$MeOC(O)C_6H_4$), 125879-57-4; 5 (Ar_1 = Ph, Ar_2 = *p*-$AcOC_6H_4$), 125879-58-5; 5 (Ar_1 = Ph, Ar_2 = *p*-HOC_6H_4), 125879-59-6; 5 (Ar_1 = Ph, Ar_2 = *p*-$MeOC_6H_4$), 125879-60-9; 5 (Ar_1 = Ar_2 = *p*-$MeOC_6H_4$), 125879-61-0; 6 (Ar_1 = Ph), 103-84-4; 7 (Ar_2 = *p*-HOC_6H_4), 103-90-2; 7 (Ar_2 = *p*-$MeOC_6H_4$), 51-66-1; 8 (Ar_1 = Ar_2 = $C_5H_{10}NC(O)$), 125879-62-1; 8 (Ar_1 = Ar_2 = Ph), 22293-38-5; 8 (Ar_1 = Ar_2 = *p*-MeC_6H_4), 125879-63-2; 8 (Ar_1 = Ar_2 = *m*-MeC_6H_4), 125879-64-3; 8 (Ar_1 = Ar_2 = *p*-ClC_6H_4), 125879-65-4; 8 (Ar_1 = Ar_2 = $C_5H_{10}NC(O)$), 125879-62-1; $Co_2(CO)_8$, 10210-68-1; Me-*m*-$C_6H_4NHNHC_6H_4$-*m*-Me, 621-26-1; Cl-*p*-$C_6H_4NHNHC_6H_4$-*p*-Cl, 953-14-0.

Thermochemistry of C–H and C–C Bond Activation: Translational Energy Dependence of Reactions of Sc^+ with Propane and 2-Butenes

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Selected reactions of Sc^+ with propane and *cis*- and *trans*-2-butene are studied by using a guided ion beam mass spectrometer. The results show reaction efficiencies at low energies of ≈100% with butene but only ≈5% with propane. The thresholds for formation of $ScCH_4^+$ and $ScC_2H_6^+$ are used to determine the two-ligand bond dissociation energies $D°(Sc^+–H) + D°(HSc^+–CH_3) = 120 \pm 2$ kcal/mol and $D°(Sc^+–CH_3) + D°(CH_3Sc^+–CH_3) = 117 \pm 2$ kcal/mol. These values are comparable to $D°(Sc^+–H) + D°(HSc^+–H) = 116 \pm 3$ kcal/mol determined previously and are consistent with bond additivity arguments based on orbital occupations in these molecules. Implications for the thermochemistry of covalent bond activation processes are discussed.

Introduction

One of the important contributions that studies of gas-phase transition metal chemistry can make to organometallic chemistry is the measurement of bond dissociation energies. At present, bond strengths between first-row transition-metal ions and one ligand (e.g., $M^+–H$, $M^+–CH_2$, and $M^+–CH_3$) are reasonably well established,[1] but far fewer bond energies are known for attachment in

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(1) Armentrout, P. B.; Georgiadis, R. *Polyhedron* 1988, *7*, 1573–1581. Armentrout, P. B.; Sunderlin, L. S.; Fisher, E. R. *Inorg. Chem.* 1989, *28*, 4436–4437.

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