Refinement was performed to convergence ($\Delta/\sigma(\max) < 0.01$) with this model. The weighting scheme was $w = [\sigma^2(F) + gF^2]^{-1}$. The final difference map was essentially featureless with all peaks less than 0.81 e Å^{-3} [near C(30)]. Inversion of configuration confirmed that the correct enantiomorph had been chosen.

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Supplementary Material Available: Listings of anisotropic thermal parameters and hydrogen atom parameters (4 pages); tables of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

Phase Transfer Catalyzed Generation of the (η^5-Cyclopentadienyl)tricarbonylhydridovanadate Anion. Applications to the Reduction of Halides, Sterically Encumbered Nitro Compounds, and the Cyclodehydration of α,β-Unsaturated Ketones

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The first examples of the application of phase transfer catalysis to early-transition-metal organometallic chemistry are described. Reaction of (η^5-cyclopentadienyl)vanadium tetracarbonyl with 5 N sodium hydroxide, benzene, and tetrabutylammonium hydrogen sulfate affords the (η^5-cyclopentadienyl)tricarbonylhydridovanadate anion. The latter is capable of effecting, under mild phase transfer conditions, the reduction of sterically encumbered nitro compounds, the semicatalytic, stereospecific, cyclodehydration of acyclic α,β-unsaturated ketones, and the reduction of the double bond of cyclic ketones, as well as the dehalogenation of a wide range of halides. The reactions may proceed via electron transfer pathways.

The use of phase transfer catalysis for the reduction of organic substrates by metal complexes has been extensively investigated in recent years. Examples include the rhodium-catalyzed hydrogenation of aromatic hydrocarbons and heterocyclic compounds,[2,3] and the conversion of nitro compounds to amines. With reference to the latter reactions, triiron dodecacarbonyl,[4] ruthenium carbonyl,[5] dichlorotris(triphenylphosphine)ruthenium(II),[6] and chloro(1,5-hexadiene)rhodium(I) dimer, together with cobalt carbonyl,[7] are effective for the phase transfer catalyzed reactions. However, none of these systems are of value when nitroarenes, containing one sizable orthosubstituent or methyl groups at the 2,6-positions, are used as substrates.

There are no examples, to our knowledge, of the use of phase transfer catalysis for reactions involving complexes of early transition metals. It seemed conceivable that commercially available cyclopentadienylvanadium tetracarbonyl (1, Cp = C_5H_5), when subjected to phase transfer conditions (aqueous base, organic phase, and quaternary ammonium salt), would experience nucleophilic attack by the quaternary ammonium hydroxide to give the vanadium anion 2 bearing a carboxyl ligand. Loss of carbon dioxide from 2 may then generate the (η^5-cyclopentadienyl)tricarbonylhydridovanadate anion (3), previously prepared by the use of sodium amalgam or dispersion techniques.[8] Synthetic applications of anionic transition-metal carbonyl hydrides have also attracted considerable recent interest,[9a] and several such anions have been synthesized by phase transfer techniques.[9b] We now wish to report that phase transfer catalysis is an excellent, experimentally simple method for the generation of the vanadium hydride 3. Furthermore, 3 is capable of reducing sterically encum-

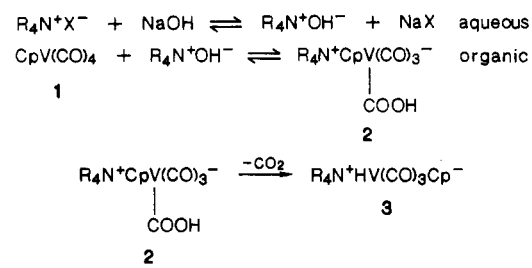

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Table I. Vanadium and Phase Transfer Catalyzed Dehalogenation of 4[a]

halide	reactn time, h	product	yield,[b] %
2-(bromomethyl)-naphthalene	0.23	2-methylnaphthalene	76
	3[c]		
	20	2-methylnaphthalene	7[d]
	0.23	2-methylnaphthalene	92[e]
1-(chloromethyl)-naphthalene	0.3	1-methylnaphthalene	74
bromodiphenyl-methane	6	diphenylmethane	62
p-chlorobenzyl chloride	6	*p*-chlorotoluene	44
p-methoxybenzyl chloride	2	*p*-methylanisole	50
o-methylbenzyl chloride	0.33	*o*-xylene	47[f]
chloromethyl phenyl sulfone	2.5	methyl phenyl sulfone	76[f]
2-chloroaceto-phenone	0.5	acetophenone	39
2-bromoaceto-phenone	0.08	acetophenone	54
β-bromostyrene	4	styrene	38
2-bromo-naphthalene	25	naphthalene	72
bromocyclohexane	16	cyclohexane	66
1-bromooctane	18	octane	60

[a] All reactions were run at 60 °C except where noted otherwise (see Experimental Section for general procedure). [b] Yields are of pure materials. Products were identified by comparison of spectral data and physical properties with those for authentic materials. [c] No $CpV(CO)_4$. [d] No phase-transfer agent. [e] Carbon monoxide atmosphere. [f] Reaction at room temperature.

bered nitro compounds and of effecting the stereospecific conversion of α,β-unsaturated ketones to 1-acyl-2-methyl-*trans*-4,5-diarylcyclopentenes.

Results and Discussion

Treatment of (η^5-cyclopentadienyl)vanadium tetracarbonyl in benzene with 5 N sodium hydroxide and tetrabutylammonium hydrogen sulfate, at room temperature and 1 atm, afforded the anionic hydridotricarbonylvanadate **3**, R = *n*-C_4H_9. Spectral data [IR (CH_3CN) ν_{CO} 1887, 1776 cm^{-1}; ^1H NMR (CD_3CN) δ 4.68 (s, 5 H, C_5H_5), −6.28 (s (br), 1 H, HV)] for **3** are in good accord with literature data for the related bis(triphenylphosphine)-nitrogen (1+) salt.[8]

Prior to effecting new chemistry with **3**, the phase transfer process was applied to the previously described dehalogenation of organic halides.[8] Reaction of a benzylic chloride or bromide (**4**, R = $ArCH_2$ or Ar_2CH; X = Cl, Br)

$$\underset{\mathbf{4}}{RX} \xrightarrow[(C_4H_9)_4N^+HSO_4^-,\ \text{room temp to 60 °C, 1 atm}]{CpV(CO)_4,\ 5\ N\ NaOH,\ C_6H_6,\ N_2} \underset{\mathbf{5}}{RH}$$

with an equimolar amount of **1**, 5 N NaOH, benzene, and tetrabutylammonium hydrogen sulfate as the phase transfer catalyst gave the reduced material in 44–76% yields (see Table I for results). The reaction is quite facile, and similar product yields were realized when an electron-donating (OCH_3) or withdrawing (Cl) substituent was present on the arene ring of a benzylic halide. The reaction can proceed at room temperature (e.g. **4**, R = *o*-$CH_3C_6H_4CH_2$, X = Cl) or at 60 °C. No reaction occurs in the absence of the vanadium carbonyl while poor product yields resulted with use of a biphasic system (i.e. no phase transfer agent).

Other activated chlorides, including chloromethyl phenyl sulfone and 2-chloroacetophenone, are also dehalogenated by **1** under the phase transfer conditions. While aryl (2-bromonaphthalene) and vinyl bromides (β-bromostyrene) react to give the corresponding debrominated products, chloroarenes such as 1-chloronaphthalene and 2-chlorothiophene are recovered unchanged after attempted reaction at 60 °C for 48 h. The reaction can be applied to aliphatic halides (e.g. 1-bromooctane).

Table II. Reduction of Nitroarenes by 1 under Phase Transfer Catalysis Conditions[a]

substrate	reactn time, min	product	yield,[b] %
nitrobenzene	15	aniline	75[c]
	80	aniline	78 (71)[d]
o-nitrotoluene	20	*o*-toluidine	83
m-nitrotoluene	25	*m*-toluidine	82
p-nitrotoluene	40	*p*-toluidine	88
o-nitroanisole	20	*o*-anisidine	85
m-nitroanisole	20	*m*-anisidine	77
p-nitroanisole	45	*p*-anisidine	74[e]
o-isopropyl-nitrobenzene	20	*o*-isopropylaniline	99 (82)
o-nitrobiphenyl	60	*o*-aminobiphenyl	94 (80)
m-nitrobi-phenyl	60	*m*-aminobiphenyl	87 (68)
2,6-dimethyl-nitrobenzene	60	2,6-dimethylaniline	98
4-nitrostilbene	10	4-aminostilbene	(76)
4-$NO_2C_6H_4$C-H=CHCO-Ph	30	4-$NH_2C_6H_4CH_2CH_2COPh$	66

[a] Reaction conditions: $CpV(CO)_4$, 5 N NaOH, C_6H_6, $(C_4H_9)_4N^+HSO_4^-$, 60 °C, 1 atm N_2; see Experimental Section for details. [b] Yields are by gas chromatography, except those in parentheses which are isolated yields. [c] 68% yield, 180 min, room temperature. [d] Using $C_{12}H_{25}N(CH_3)_2C_2H_5^+Br^-$ as the phase transfer catalyst. [e] 11% in the absence of $(C_4H_9)_4N^+HSO_4^-$ (180 min, 60 °C).

The phase transfer dehalogenation of halides, like the homogeneous reaction, probably occurs by a radical pathway. If one uses 6-bromo-1-hexene as the reactant, then 1-hexene and methylcyclopentane are formed in a ratio of 0.77, consistent with the intermediacy of a radical species.[8]

With the knowledge that the vanadium hydride is able to dehalogenate a variety of organic compounds under phase transfer conditions, the biphasic system was employed for other reduction reactions. The hydride **3**, generated in situ, is an excellent reagent for the reduction of nitroarenes to aromatic amines in fine yields (Table II). What is particularly significant about this facile reductive process is its utilization for the conversion of ortho-substituted nitro compounds including those containing a bulky substituent (e.g. phenyl, isopropyl) at the 2-position of a benzene ring or methyl groups at the 2- and 6-positions (e.g. 2,6-dimethylnitrobenzene). This method is superior to the use of other transition-metal hydrides for the reduction of such nitro compounds. Poor product yields resulted when these reactions were effected in the absence of the phase transfer agent. The reduction can occur in the presence of ether or olefinic substituents, while the double bond of an α,β-unsaturated ketone functionality is also reduced.

The reactivity of the sterically encumbered nitro compounds is high with reactions being complete within an hour at 60 °C and 1 atm. Nevertheless, nitrobenzene and nitroarenes containing substituents at the meta or para positions are usually more reactive than substrates having one or more ortho substituents. For instance, comparison of the proportion of amines formed from *p*-nitrotoluene and from 2,6-dimethylnitrobenzene indicates that the initial reaction rate for *p*-nitrotoluene is greater than that for 2,6-dimethylnitrobenzene (Figure 1). However, with

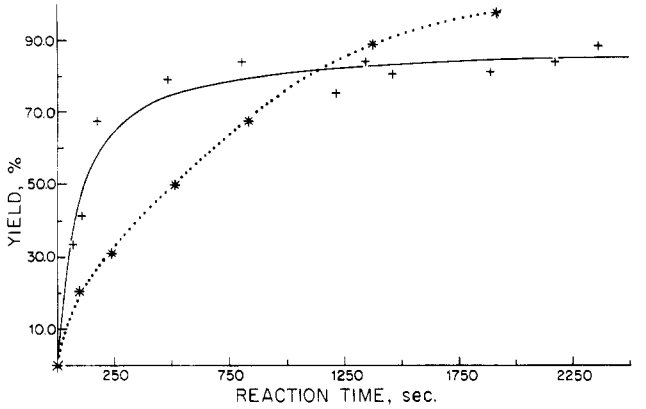

Figure 1. Plot of the percent yield of amines, as a function of time (seconds), in the reaction of 1:1 *p*-nitrotoluene:$CpV(CO)_4$ and 1:1 2,6-dimethylnitrobenzene:$CpV(CO)_4$ [*p*-toluidine (+); 2,6-dimethylaniline (*)].

time, 2,6-dimethylnitrobenzene undergoes greater reduction than *p*-nitrotoluene. In addition, if one treats nitrobenzene and 2,6-dimethylnitrobenzene (1:1 ratio) with an equimolar amount of **1** for 30 min under the usual phase transfer conditions, aniline is formed in 72% yield while 2,6-dimethylnitrobenzene is recovered unchanged. The greater reactivity of nitrobenzene may be due, in part, to the higher reduction potential of nitrobenzene ($E_{1/2}$ = −0.62 V) compared with that of 2,6-dimethylnitrobenzene ($E_{1/2}$ = −0.73 V).[10] However, that reduction potential is not the sole factor (steric effects as well as the ease of electron transfer may be important) affecting reactivity was demonstrated by using two nitro compounds having almost the same reduction potential. Use of a 1:1:1 ratio of nitrobenzene ($E_{1/2}$ = −0.62 V), *o*-isopropylnitrobenzene ($E_{1/2}$ = 0.61 V) and **1** for 1 h resulted in 94% conversion of nitrobenzene while *o*-isopropylaniline was obtained in only 25% yield.

A mechanism proposed for the reduction of nitro compounds is outlined in Scheme I. Electron transfer from the vanadium hydride **3** to the nitro reactant would give the nitroaromatic radical anion **6** and the organo vanadium radical **7**. Precedence exists for the generation and reactivity of such nitroaromatic radical anions in aqueous solutions.[11] Hydrogen atom transfer can then occur to give **9** and **8**, the latter collapsing to the nitrosoarene **10** and hydroxide ion.[12] A hydridovanadium dicarbonyl anion (**11**), formed by reaction of **9** with hydroxide ion, can then undergo electron and hydrogen atom transfer to give ArNOH$^-$ (**12**) and $CpV(CO)_2$ (**13**). A nitrene, if generated from **12**, may react with **13** to form complex **14**. Hydroxide ion attack on **14** would afford **15** and then **16** by hydrogen transfer. The amine may then arise either by protonation of **16** followed by reductive elimination (path a) or by reaction with hydroxide ion, followed again by reductive elimination (path b).

The result obtained using 3-(*p*-nitrophenyl)-1-phenyl-2-propen-1-one, i.e. reduction of both the nitro group and the double bond of the α,β-unsaturated ketone, indicated that the vanadium hydride may be an active reagent for the hydrogenation of the double bond of α,β-unsaturated ketones. Indeed, when 2-cyclohexen-1-one was treated with an equimolar amount of cyclopentadienylvanadium tetracarbonyl (**1**) under phase transfer conditions [5 N NaOH, C_6H_6, $(C_4H_9)_4N^+HSO_4^-$(N_2)] for 15 min at 60 °C, cyclohexanone was formed in 82% yield. In contrast, no

Scheme I

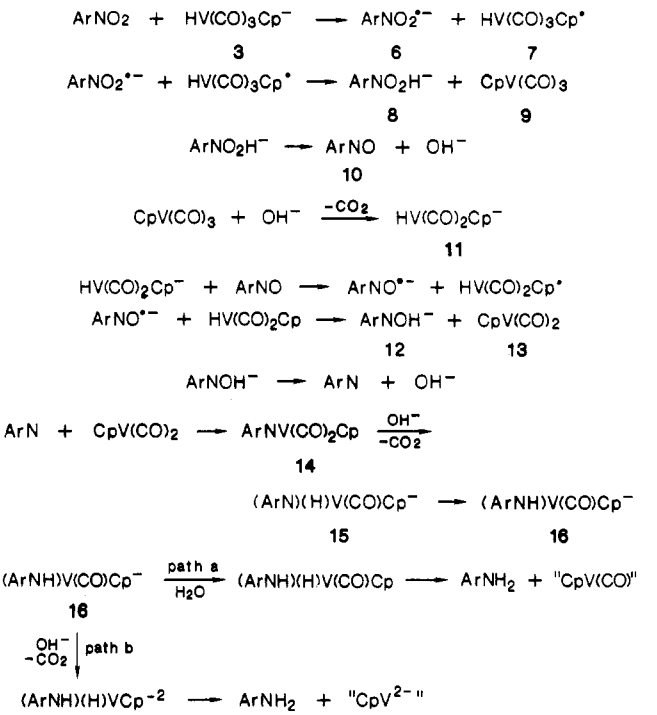

Table III. Synthesis of 21 from 20 and 1 Using Phase Transfer Conditions

ArCH=CHCO-CH_3, Ar =	ratio of 20:1	reactn time, h	yield of products, % 21	22
Ph	3.3	0.16	70	21
	2.9	20.5[a]	44	5
		0.25[b]	74	18
p-ClC_6H_4	4.7	1.0	71	9
p-$CH_3OC_6H_4$	4.3	1.0	68	32
3,4-$(CH_3O)_2C_6H_3$	4.1	1.3	76	24
p-$CH_3C_6H_4$	6.3	2.0[b]	87	13
	8.6	20	68	13
2,4-$(CH_3)_2C_6H_3$	4.1	2.0	34	25

[a] Room temperature. [b] CO atmosphere.

reduction of 2-cyclohexen-1-one occurs with $HV(CO)_3Cp^-$, under homogeneous conditions, for 60 min at 25 °C.[8] Application of the phase transfer process to 2-cyclopenten-1-one gave cyclopentanone in 80% yield.

If 1,3-diphenyl-2-propen-1-one (benzylideneacetophenone) is reacted with **1** for 40 min, then the saturated ketone **17** is formed, but in 23% yield of isolated product. Appreciable quantities of the dimeric 1,6-diketone 1,3,4,6-tetraphenylhexane-1,6-dione (**18**, 17%)[13] and the cyclopentanol **19** (11%)[14] were also isolated from this reaction. If one assumes that **18** is generated by a pathway

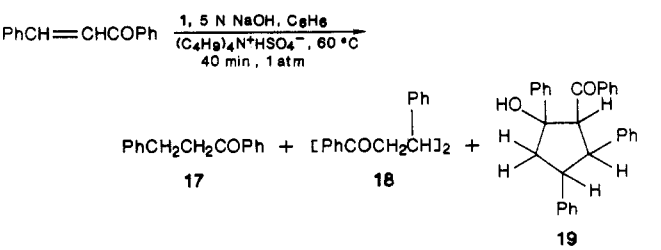

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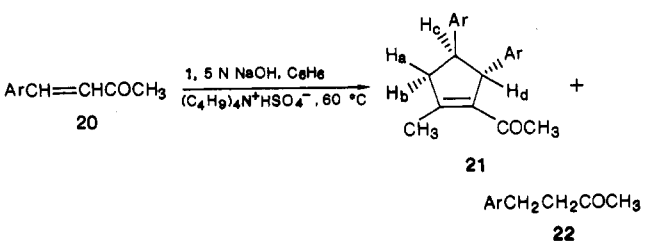
Table IV. Pertinent Spectral Data for 21

21, Ar =	^{1}H NMR,[a] δ	^{13}C NMR,[b] δ	MS, *m/e* [M$^+$]
Ph	1.83 (s, 3 H, $COCH_3$), 2.18 (m, 3 H, CH_3), 2.66 (dd, 1 H, H_a), 3.03 (dd, 1 H, H_b), 3.16 (m, 1 H, H_c), 4.19 (m, 1 H, H_d), 7.00–7.30 (m, 10 H, Ph)		276
p-$CH_3OC_6H_4$	1.87 (s, 3 H, $COCH_3$), 2.17 (m, 3 H, CH_3), 2.59 (dd, 1 H, H_a), 2.96 (dd, 1 H, H_b), 3.08 (m, 1 H, H_c), 3.76 (s, 3 H, OCH_3), 4.07 (m, 1 H, H_d), 6.74–7.05 (m, 8 H, aromatic protons)	16.62 (CH_3), 30.03 ($COCH_3$) 47.19 (CH_2), 52.56 (CH), 55.17, 55.22 (OCH_3), 61.50 (CH), 113.85, 114.04, 127.96, 128.19, 136.48, 136.83, 138.11, 152.78, 158.14, 158.23 (olefinic and aromatic carbons), 199.39 (CO)	336
p-ClC_6H_4	1.89 (s, 3 H, $COCH_3$), 2.27 (m, 3 H, CH_3), 2.59–3.13 (m, 3 H, H_{a-c}), 4.11 (m, 1 H, H_d), 6.93–7.26 (m, 8 H, aromatic protons)		344, 346, 348
2,4-$(CH_3)_2C_6H_3$	1.87 (s, 3 H, $COCH_3$), 2.18 (m, 3 H, CH_3), 2.17, 2.19, 2.23, 2.26 (s, each 12 H, CH_3's on aromatic rings), 2.50 (dd, 1 H, H_a), 3.01 (dd, 1 H, H_b), 3.34 (m, 1 H, H_c), 4.26 (m, 1 H, H_d), 6.85–7.26 (m, 6 H, aromatic protons)	16.75 (olefinic CH_3), 19.42, 19.60, 20.86, 20.92 (aromatic methyls), 29.76 ($COCH_3$), 47.32 (CH_2), 47.61 (CH), 56.91 (CH), 125.61, 125.91, 127.09, 127.23, 130.98, 131.18, 135.23, 135.28, 135.46, 135.64, 138.32, 139.97, 140.82, 153.20 (olefinic and aromatic carbons) 199.02 (CO)	332
p-$CH_3C_6H_4$	1.86 (s, 3 H, $COCH_3$), 2.26, 2.29, 2.38 (s, each, 9 H, methyls), 2.59 (dd, 1 H, H_a), 2.99 (dd, 1 H, H_b), 3.11 (m, 1 H, H_c), 4.11 (m, 1 H, H_d), 6.89–7.09 (m, 8 H, aromatic protons)	16.63 (olefinic CH_3), 20.97, 21.02 (aromatic methyls), 47.36 (CH_2), 52.67 (CH), 61.79 (CH), 126.86, 126.95, 129.22, 129.39, 135.92, 136.05, 137.93, 141.42, 142.03, 153.10 (olefinic and aromatic carbons), 199.26 (CO)	304

[a] $CDCl_3$ with tetramethylsilane as internal standard. Structural assignments are based on COSY and other decoupling experiments. [b] $CDCl_3$ with tetramethylsilane as the internal standard.

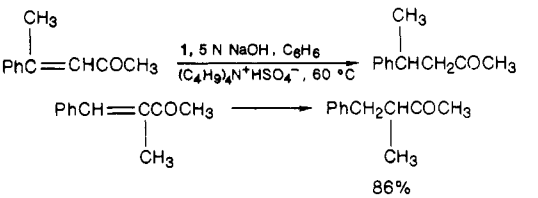
involving a benzylic radical and that **19** is formed from **18** under the basic conditions (i.e. **1** is required for forming **17** and **18**, but not for the cyclization reaction), then replacement of the benzoyl unit for the reactant by acyl should result in a more facile route to compounds of structural type **19** or their dehydrated analogues. Use of **20**, Ar = Ph, as the substrate afforded 1-acyl-2-methyl-*trans*-4,5-diphenylcyclopentene (**21**, Ar = Ph) in 70% yield, together with 21% of the saturated ketone **22** (Ar = Ph).



Only traces of products were detected when the reaction was effected without the phase transfer agent, while neither **21** nor **22** was formed in the absence of the vanadium complex **1**. Use of carbon monoxide instead of nitrogen has little influence on the reaction of **20**. One can run the reaction of **20** with **1** at room temperature rather than at 60 °C but at an appreciably reduced rate. It is interesting to note that the analogue of **19** was formed when the reaction of benzylideneacetophenone was repeated by using 100 mL instead of 25 mL of benzene (i.e. lower effective base concentration).

trans-Diarylcyclopentenes (**21**) were isolated as the principal products from reaction of a series of unsaturated ketones of structural type **20** in which the arene ring contained an electron-donating or -withdrawing group (see Table III for results). The stereochemistry of **21** was established on the basis of nuclear magnetic resonance[15] and mass spectral data (Table IV) and an X-ray analysis of **21** [Ar = 2,4-$(CH_3)_2C_6H_3$] (to be published separately). Note that these reductive cyclization reactions are semicatalytic in nature with substrate:1 ratios being as high as 8.6:1.0 (Table III).

Finally, the presence of a methyl substituent on the double bond of **20** results in the reduction of the unsaturated function.



In Scheme II is outlined a possible mechanism for the reaction of **20** with in situ generated **3**. Single electron transfer from the hydride **3** to **20** would generate the radical anion **23** and **7**. Hydrogen atom transfer may then occur (path a) affording **9** and **24**. Protonation of the latter would give **22** (via **25**). An alternate reaction course (path b) is the dimerization of **23** to **26** followed by protonation (**27**) and tautomerism to **28**. Base-induced cyclodehydration of **28** would result in the formation of **21**. Finally, **23** can experience a second electron transfer affording **29** which can undergo Michael addition to the substrate **20** giving **26** (path c).

In conclusion, phase transfer catalysis enables one to generate $CpV(CO)_3H^-$ under remarkably simple conditions. This methodology avoids the requirements for anhydrous, inert-atmosphere conditions or the use of amalgam or dispersion techniques. This research has demonstrated the utility of the hydride as an excellent reagent for the reduction of hindered nitro compounds, the stereospecific, semicatalytic, cyclodehydration of acyclic α,β-unsaturated ketones with cyclic ketones undergoing double bond reduction (not observed under homogeneous conditions), and the dehalogenation of a wide range of halides. These are the first examples of the use of phase transfer catalysis in the area of early-transition-metal chemistry.

Experimental Section

Melting point determinations were made by using a Fisher-Johns apparatus. Gas chromatographic determinations were made

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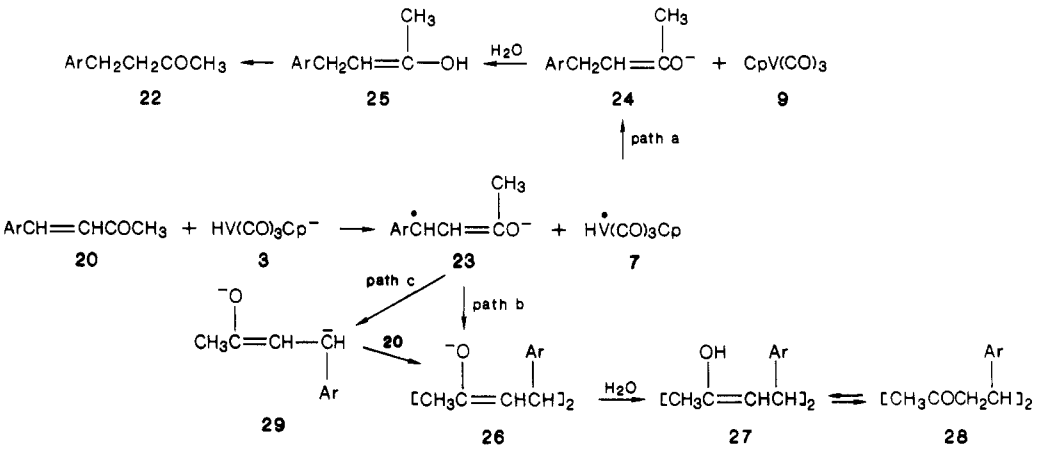
Scheme II



on a Varian Vista 6000, 3300, or 3400 chromatograph. Columns used for analysis included 3% OV-17 or OV-101 on Chromosorb W or a DB1 megabore column. Proton and carbon-13 magnetic resonance spectra were recorded on a Varian XL-300 spectrometer. A VG-7070E spectrometer was used for mass spectral determinations, and infrared spectra were recorded on a Perkin-Elmer 783 spectrometer.

All of the organic reactants were purchased from commercial sources and were used as received. Cyclopentadienylvanadium tetracarbonyl was either prepared following a literature procedure[16] or purchased from Strem Chemical Co. Solvents were purified by standard methods.

Generation of $(C_4H_9)_4N^+CpV(CO)_3H^-$. A mixture of 0.228 g (1.0 mmol) of cyclopentadienylvanadium tetracarbonyl in benzene (10 mL) and 0.363 g (1.10 mmol) of tetrabutylammonium hydrogen sulfate in 5 N sodium hydroxide (10 mL) was stirred overnight at room temperature. The phases were separated, and the organic phase was concentrated affording a yellow solid. The latter was filtered, washed with water (3 × 10 ml) and cold ether, and then vacuum dried to give bright yellow $(C_4H_9)_4N^+CpV(CO)_3H^-$ in 87% yield: IR (CH_3CN) ν_{CO} 1887, 1776 cm^{-1}; ^1H NMR (CD_3CN) δ 4.68 (s, 5 H, C_5H_5), −6.28 (s (br), 1 H, HV).

General Procedure for the Reaction of Halides with $CpV(CO)_4$. Nitrogen was bubbled for 15 min through a mixture of benzene (10 mL) and 5 N NaOH (10 mL) containing 0.85 g (0.25 mmol) of tetrabutylammonium hydrogen sulfate. Cyclopentadienylvanadium tetracarbonyl (0.228 g, 1.0 mmol) was added, and the temperature of the stirred mixture was gradually increased to 60 °C. The halide (1.0 mmol) was added, and the reaction mixture was stirred for the period indicated in Table I. During the course of the reaction, the organic phase turns from orange to a pale color. The phases were separated; the organic phase was washed with brine, dried (Na_2SO_4), and concentrated by rotary evaporation to give the product. Purification, if required, was effected by preparative thin-layer chromatography (silica gel) or by distillation.

General Procedure for the Reduction of Nitroarenes by $CpV(CO)_4$. Except for the use of the nitro reactant instead of halide, the procedure was identical with that described for the halide–vanadium reaction. For competition experiments with two different nitro compounds at the same time, the usual procedure was followed with the presence of 1.0 mmol of the second nitro compound.

General Procedure for the Reaction of α,β-Unsaturated Ketones with $CpV(CO)_4$. The procedure described for the halide reaction was followed, with the following modifications: 1.0 mmol of the α,β-unsaturated ketone was used instead of halide, and less than 1.0 mmol of cyclopentadienylvanadium tetracarbonyl was used (see Table III). When 1,3-diphenyl-2-propen-1-one was employed as the reactant, the products **17**–**19** were separated by using a Harrison 7924 chromatotron. Preparative thin-layer chromatography (silica gel) with 5:1 hexane/ethyl acetate as the developing solvent system was used to isolate pure products from all other reactions involving α,β-unsaturated carbonyls.

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Registry No. **1**, 12108-04-2; **3** (R = C_4H_9), 116926-71-7; **17**, 1083-30-3; **18**, 7028-45-7; **19**, 33418-22-3; **20** (Ar = Ph), 122-57-6; **20** (Ar = p-ClC_6H_4), 3160-40-5; **20** (Ar = p-$CH_3OC_6H_4$), 943-88-4; **20** (Ar = 3,4-$(CH_3O)_2C_6H_3$, 15001-27-1; **20** (Ar = p-$CH_3C_6H_4$), 3160-38-1; **20** (Ar = 2,4$(CH_3)_2C_6H_3$), 55793-96-9; **21** (Ar = Ph), 33525-38-1; **21** (Ar = p-ClC_6H_4), 116910-96-4; **21** (Ar = p-$CH_3OC_6H_4$), 116910-97-5; **21** (Ar = 3,4-$(CH_3O)_2C_6H_3$), 116910-98-6; **21** (Ar = p-$CH_3C_6H_4$), 116910-99-7; **21** (Ar = 2,4-$(CH_3)_2C_6H_3$), 116911-00-3; **22** (Ar = Ph), 2550-26-7; **22** (Ar = p-ClC_6H_4), 3506-75-0; **22** (Ar = p-$CH_3OC_6H_4$), 104-20-1; **22** (Ar = 3,4-$(CH_3O)_2C_6H_3$), 6302-60-9; **22** (Ar = p-$CH_3C_6H_4$), 7774-79-0; **22** (Ar = 2,4-$(CH_3)_2C_6H_3$, 55793-97-0; CH_2=$CH(CH_2)_3CH_2Br$, 2695-47-8; CH_2=$CH(CH_2)_3CH_3$, 592-41-6; p-$O_2NC_6H_4CH$=$CHCOPh$, 1222-98-6; $(Ph)_2CHBr$, 776-74-9; p-$ClC_6H_4CH_2Cl$, 104-83-6; p-$MeOC_6H_4CH_2Cl$, 824-94-2; o-$CH_3C_6H_4CH_2Cl$, 552-45-4; o-$ClC_6H_4COCH_3$, 532-27-4; o-$BrC_6H_4COCH_3$, 70-11-1; PhCH=CHBr, 103-64-0; $CH_3(CH_2)_6CH_2Br$, 111-83-1; $(Ph)_2CH_2$, 101-81-5; p-$CH_3C_6H_4Cl$, 106-43-4; p-$CH_3C_6H_4OCH_3$, 104-93-8; o-$CH_3C_6H_4CH_3$, 95-47-6; $PhCOCH_3$, 98-86-2; PhCH=CH_2, 100-42-5; $CH_3(CH_2)_6CH_3$, 111-65-9; $PhNO_2$, 98-95-3; o-$CH_3C_6H_4NO_2$, 88-72-2; m-$CH_3C_6H_4NO_2$, 99-08-1; p-$CH_3C_6H_4NO_2$, 99-99-0; o-$CH_3OC_6H_4NO_2$, 91-23-6; m-$CH_3OC_6H_4NO_2$, 555-03-3; p-$CH_3OC_6H_4NO_2$, 100-17-4; o-$(CH_3)_2CHC_6H_4NO_2$, 6526-72-3; o-$PhC_6H_4NO_2$, 86-00-0; m-$PhC_6H_4NO_2$, 2113-58-8; 2,6-$(Me)_2C_6H_3NO_2$, 81-20-9; p-$NO_2C_6H_4CH$=$CHPh$, 4003-94-5; p-$NO_2C_6H_4CH$=$CHCOPh$, 1222-98-6; $PhNH_2$, 62-53-3; o-$CH_3C_6H_4NH_2$, 95-53-4; m-$CH_3C_6H_4NH_2$, 108-44-1; p-$CH_3C_6H_4NH_2$, 106-49-0; o-$CH_3OC_6H_4NH_2$, 90-04-0; m-$CH_3OC_6H_4NH_2$, 536-90-3; p-$CH_3OC_6H_4NH_2$, 104-94-9; o-$(CH_3)_2CHC_6H_4NH_2$, 643-28-7; o-$PhC_6H_4NH_2$, 90-41-5; m-$PhC_6H_4NH_2$, 2243-47-2; 2,6-$(Me)_2C_6H_3NH_2$, 87-62-7; p-$NH_2C_6H_4CH_2CH_2COPh$, 59276-79-8; methylcyclopentane, 96-37-7; 2-cyclohexen-1-one, 930-68-7; cyclohexanone, 108-94-1; 2-cyclopenten-1-one, 930-30-3; cyclopentanone, 120-92-3; benzylideneacetophenone, 94-41-7; 2-(bromomethyl)naphthalene, 939-26-4; 1-(chloromethyl)naphthalene, 86-52-2; chloromethyl phenyl sulfone, 7205-98-3; 2-bromonaphthalene, 580-13-2; bromocyclohexane, 108-85-0; 2-methylnaphthalene, 91-57-6; 1-methylnaphthalene, 90-12-0; methyl phenyl sulfone, 3112-85-4; naphthalene, 91-20-3; cyclohexane, 110-82-7.

(16) King, R. B. *Organomet. Synth.* **1965**, *1*, 105.