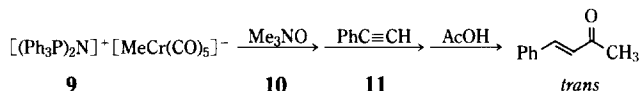
**Table 1.** Hydroacylation of phenylacetylene with PPN Salt 9

Entry	9		10		11		Yield ^a
	equiv	equiv	Rxn Temp	equiv	Rxn Temp		
1	1.0	—		1.0	rt	17%	
2	1.0	1.0	0°C	1.0	rt	41%	
3	1.0	1.0	0°C	1.0	rt ^b	39%	
4	1.0	1.0	rt	1.0	rt	38%	
5	1.5	—		1.0	rt ^c	34%	
6	2.0	3.1	-78°C	1.0	-78°C -0°C	48%	
7	2.0	4.0	0°C	1.0	rt	48%	

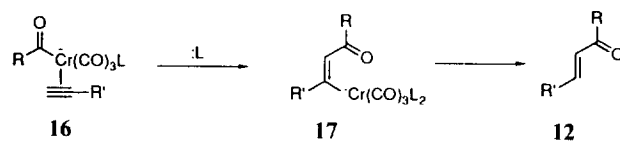
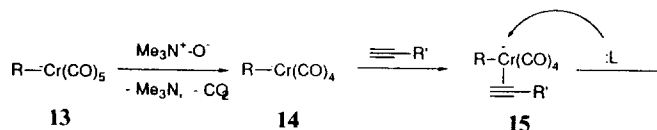
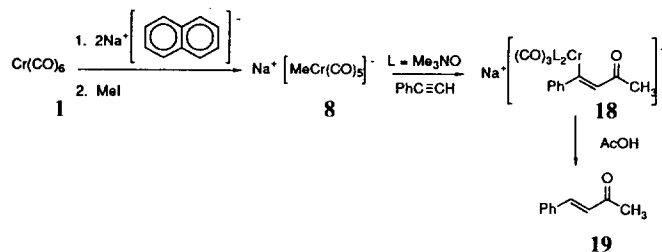
^a Isolated yields based on phenylacetylene. ^b Work-up with dilute HCl (0.1 N 25 ml) and dilute AcOH (0.1 N 25 ml) was used in other cases. ^c Under 100,000 psi.

Results and Discussion

First, in order to find out the optimum condition of hydroacylation of alkynes with alkylpentacarbonylchromate, bis(triphenylphosphoranylidene)ammonium (PPN) salt of alkylpentacarbonylchromate anion was prepared in THF solution: The reaction of chromium hexacarbonyl **1** with sodium naphthalenide **2** at -78°C gave a dark suspension, which was warmed up to ambient temperature to give a dark orange clean solution of disodium pentacarbonylchromate **3**.⁵ Subsequent methylation with excess methyl iodide at room temperature provided sodium methylpentacarbonylchromate **8**. The corresponding PPN salt **9** was obtained in moderate yield by the addition of bis(triphenylphosphoranylidene)ammonium chloride (PPN⁺Cl⁻) to the resulting yellow solution (Scheme 2).

Our initial study was focused on the feasibility of conversion of the methylpentacarbonylchromate anion **9** to an acyl metal species, which might behave as a source of acyl moiety upon interaction with unsaturated organic compounds such as alkynes. Reaction of phenylacetylene **11** as a model substrate with the PPN salt **9** with varying stoichiometries in the presence of some additives was studied under various conditions. Thus, this reaction even without any additive did provide *trans*-4-phenyl-3-buten-2-one **12**, albeit in 17% yield. *cis*-Isomer could not be detected in all cases. Addition of trimethylamine N-oxide **10** improved the yield slightly but not much to a synthetically useful level. The results are shown in Table 1.

The idea of addition of trimethylamine N-oxide **10** was to make it more facile in the coordination of phenylacetylene to the vacant coordination site created by expulsion as CO₂ of one of the carbonyl group of metal carbonyl.⁷ (Scheme 3)

**Scheme 3.****Scheme 4.****Table 2.** Hydroacylation of Phenylacetylene with *in situ* generated Sodium Methylpentacarbonylchromate

Entry	Cr(CO) ₆ ^a (equiv)	PhC≡CH (equiv)	Rxn Temp.	Additive (equiv)	Yield ^c
1	2	1		Me ₃ NO (2)	32%
2	4	1	-78°C -rt	Me ₃ NO (1)	21%
3	4	1		Me ₃ NO (4)	56%
4	4	1	rt	NMNO ^b (4)	74%

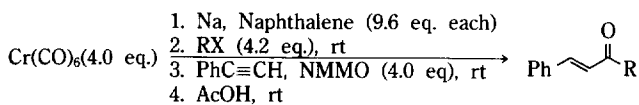
^a Naphthalenide was added to the solution of Cr(CO)₆ at -78°C .

^b NMNO: N-Methylmorpholine N-oxide. ^c Isolated Yields based on phenylacetylene.

Unfortunately, various equivalents of trimethylamine N-oxide did not provide much difference and gave again low yields as shown in Entries 2, 6, and 7 of Table 1.

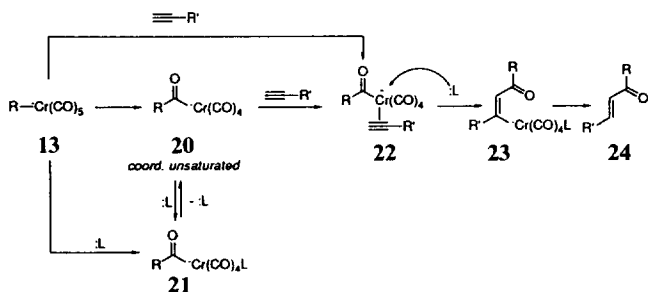
Thus another approach was investigated to develop a new hydroacylation procedure, where the *in situ* generated methylpentacarbonylchromate complex was used to prevent the effect of bulky PPN cation (Scheme 4). A practical advantage of this approach appears to be the avoidance of isolation of metallic species such as **3**, which was moisture and oxygen sensitive. Various conditions of the hydroacylation of phenylacetylene with *in situ* generated methylpentacarbonylchromate **3** were examined, and the proper condition of this reaction was obtained (Entry 4). And N-methylmorpholine N-oxide, instead of trimethylamine N-oxide, gave higher yields. These results of optimization are summarized in Table 2.

Having succeeded in developing a proper condition with methyl iodide, reactions of the dianion with other alkyl halides and subsequent reactions with phenylacetylene were carried out. Good yields were obtained in the reaction of primary alkyl halide, but the reaction of secondary alkyl halide gave poor yield (Entry 7 in Table 3) as expected, presumably due to the low reactivity of the secondary alkyl halide for

Table 3. Hydroacylation of Phenylacetylene with Various *in situ* Generated Alkylpentacarbonylchromate Complexes in the Presence of NMMO

Entry	RX	Product	Yield ^a
1	MeI	<i>trans</i> -MeCOCH=CHPh	74%
2	MeI	<i>trans</i> -MeCOCH=CHPh	56% ^b
3	MeI	<i>trans</i> -MeCOCH=CHPh	68% ^c
4	<i>n</i> -PrBr	<i>trans</i> - <i>n</i> -PrCOCH=CHPh	51%
5	<i>n</i> -BuI	<i>trans</i> - <i>n</i> -BuCOCH=CHPh	75%
6	<i>n</i> -OctBr	<i>trans</i> - <i>n</i> -OctCOCH=CHPh	44%
7	<i>i</i> -BuCl	<i>trans</i> - <i>i</i> -BuCOCH=CHPh	7%

^a Isolated yields based on phenylacetylene. ^b Me₃N-O was used instead of NMMO. ^c *t*-BuOO⁻Li⁺ was used in place of NMMO.

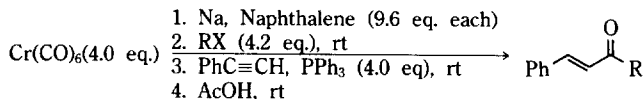
**Scheme 5.**

the nucleophilic oxidative addition and high tendency to E2 reaction (step a in Scheme 1). The results are shown in Table 3.

As mentioned earlier, even in the presence of trimethylamine N-oxide, treatment of phenylacetylene with the PPN salt **4** gave the product in low yield. A way of looking at it is that migratory insertion of an alkyl group to a carbon monoxide on chromium precedes coordination of phenylacetylene. With that assumption in hand, the overall reaction may proceed along the path shown in Scheme 5. Also, it is to be noted that extra ligands may be necessary in two migratory insertion steps, namely migratory insertion of an alkyl group to coordinated carbon monoxide and that of an acyl group to coordinated alkyne.

In this regard, it was shown that square pyramidal acylmanganese complex **25** are configurationally stable for low spin complex and have unoccupied site for ligand.⁸ The acyltetra-carbonylchromate anion complexes **26**, which were generated by the migratory insertion of metal carbonyl to alkyl ligands in the complexes of alkylpentacarbonylchromate complexes, were isoelectronic with **25** and thus presumed to have the same structure.

Thus, subsequent efforts were focused on finding a suitable entering ligand which is able to accelerate the migratory insertion steps. As shown in the Scheme 5, the vacant site which was generated by the migration of acyl moiety had to be occupied by incoming ligand. It was assumed that tri-

Table 4. Effect of PPh₃ in Hydroacylation of Phenylacetylene with Various Alkylpentacarbonylchromate Complexes

Entry	RX	Product	Yield ^a
1	MeI	<i>trans</i> -MeCOCH=CHPh	89%
2	<i>n</i> -PrBr	<i>trans</i> - <i>n</i> -PrCOCH=CHPh	72%
3	<i>n</i> -BuI	<i>trans</i> - <i>n</i> -BuCOCH=CHPh	88%
4	<i>n</i> -OctI	<i>trans</i> - <i>n</i> -OctCOCH=CHPh	71%
5	<i>i</i> -BuCl	<i>trans</i> - <i>i</i> -BuCOCH=CHPh	46%

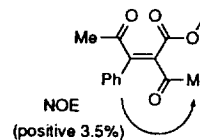
^a Isolated yields based on phenylacetylene.

Table 5. Hydroacylation of Functionalized Alkynes with *in situ* Prepared Sodium Methylpentacarbonylchromate

Entry	Alkyne	Products	Yield ^a
1	<i>n</i> -C ₄ H ₉ C≡CCO ₂ Et	(27) ^r	32% ^b
2	<i>n</i> -C ₄ H ₉ C≡CCO ₂ Et	(28) ^r	10% ^c
3	PhC≡CCO ₂ Et	(28) ^r	52% ^b
4	PhC≡CCO ₂ Et	(28) ^r	35% ^c
5	1-Dodecyne		47% ^b
6	1-Dodecyne	(29)	33% ^c
7	1-Dodecyne	(29)	22% ^d

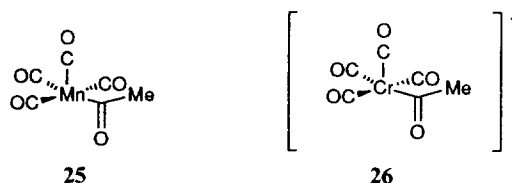
^a Isolated yields based on alkynes. ^b PPh₃ was used as an additive. ^c NMMO was used as an additive. ^d *t*-BuOO⁻Li⁺ was used as an additive. ^r In the NOE differential spectrum positive effect was observed between vinyl proton and protons of acetyl group. [†] The spectral data of this compound, **28**, are given below.

IR: 1815 (s), 1710 (s), 1662 (s) cm⁻¹. ¹H-NMR: δ 7.3 (m, 5H), 4.13 (q, 2H), 2.52 (s, 3H), 1.90 (s, 3H), 1.12 (t, 3H). ¹³C-NMR: δ 178.15 (C=O), 167.13 (C=O), 162.91 (C=O), 138.56 (Ph), 128.71 (Ph), 127.88 (Ph), 126.29 (Ph), 115.89 (?), 60.11 (OCH₂), 51.98 (?), 21.69 (Me), 13.74 (Me), 13.67 (OCH₂CH₃). GC-MS (relative intensity) 260 (M, 31), 217 (M-COMe, 77), 189 (M-COMe-CO, 45), 159 (M-CO-CO₂Et, 90), 43 (COCH₃, 100).



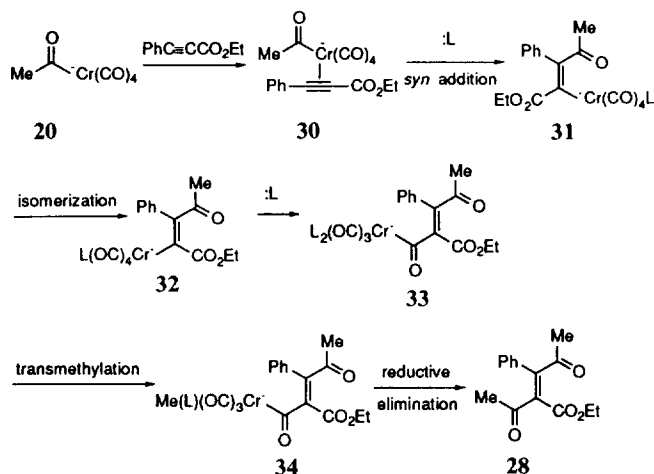
phenylphosphine might be able to play this role. Gratifyingly, the desired products were obtained in good yield (Table 4).

To show the applicability of this reaction to a wide variety of alkynes, several alkynes having other functional groups



were investigated but only moderate yields were obtained (Table 5).

In these cases especially with conjugated alkyne, instead of hydroacylation, some double acylation has occurred. Thus, when ethyl phenylpropiolate was subjected to the same reaction condition, a double acylated product **28** was obtained. The formation of this compound can be rationalized as following.



This reaction was surprising in two aspects: The second migratory insertion reaction of acyl group to coordinated alkyne in the usual *syn* manner was followed by *Z* to *E* isomerization, which was not observed with simple alkynes. Secondly, it is not clear at this moment the source of methyl group in the second acetyl group. One thing that is clear is that the methyl group was not originated from excess methyl iodide. In one of experiments, after methylation of disodium pentacarbonylchromate with methyl iodide, all the solvents were evaporated off to get rid of excess methyl iodide which might be present. Addition of fresh solvent (THF) and subsequent reaction with ethyl phenylpropiolate under otherwise same condition again provided the doubly acetylated product **28**. Clearly, some more fundamental insight on this reaction is needed.

Experimental

General. Small- and medium-scale purifications (20 mg-2 g) were performed by radial chromatography by using Harrison Research Chromatotrons on plates of 1-, 2-, or 4-mm thickness made with Merck silica 60 PF₂₅₄ containing gypsum. Flash chromatography was performed on a Tokyo Rikagikai EF-10 with Merck 230-400 mesh silica gel. ¹H-NMR was obtained on a Varian EM-360A (60 MHz) or a Varian Gemini 300 (300 MHz) spectrometer. NMR Spectra were recorded in ppm (δ) relative to Me₄Si (δ 0.00) as an internal standard unless stated otherwise and are reported as follows: chemical shift, multiplicity (br=broad, s=singlet, d=doublet, t=triplet, q=quartet), coupling constant and integration. Infrared spectra were obtained on a Shimadzu IR-400 or Mattson Galaxy 2000 spectrometers. All reactions involving organometallic reagents were carried out under an inert atmosphere of nitrogen or argon. Solvents and liquid reagents were transferred using hypodermic syringes or double ended

needle. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl under a nitrogen atmosphere just prior to use. Chromium hexacarbonyl (Strem chemicals inc.), naphthalene (Baker), sodium lump (Fluka), phenylacetylene (Aldrich), methyl iodide (Aldrich), and other alkyl halides (Aldrich) were obtained from commercial suppliers and used without further purifications. The following chemicals were prepared according to the literature procedure:⁹ 1-dodecyne, ethyl phenylpropiolate, ethyl 2-heptynoate.

Preparation of Disodium Pentacarbonylchromate Dianion (3). To sodium (0.45 g, 19.6 mmol) in THF (38 ml) placed in a thoroughly dried 50 mL round bottomed flask, naphthalene (2.46 g, 19.2 mmol) was added under nitrogen. Dark green color appeared instantaneously as naphthalene dissolved, and the solution of mixture was stirred for 2 h. The THF solution of naphthalenide was transferred under nitrogen to the suspension of chromium hexacarbonyl (1.76 g, 8 mmol) in THF (10 ml) in another 100 ml round bottomed flask over 1 h at -78°C and the newly formed dark suspension of mixture was allowed to warm up to room temperature and stirred for 4 h to give a clear and dark brown solution which was ready for further synthesis. IR (in THF) 1817(s), 1769(s) cm^{-1} .

Preparation of PPN Salt of Methylpentacarbonylchromate Complex (4). To dark yellow solution of 5 mmol of (3), was added excess methyl iodide through a hypodermic syringe and the solution of mixture was stirred for 1 h. A solution of PPN Cl (2.99 g, 5.2 mmol) dissolved in MC (25 ml) was transferred to the resulting solution at room temperature and stirred overnight. Solvent was evaporated to give dark yellow solid. Recrystallization of this solid gave 2.54 g (68%) of desired product (4). IR (KBr) 2017, 1923, 1884, 1840 cm^{-1} . NMR (Aceton-d₆/MC) δ 8.5 (s, 30H), -2.0 (s, 3H).

Reaction of (4) with Phenylacetylene. To the PPN salt (4) (2.98 g, 4 mmol), dissolved in 20 ml of THF in a 50 ml round bottomed flask equipped with a magnetic stirring bar, a septum inlet and a nitrogen-filled balloon, was added 0.22 ml of phenylacetylene (2 mmol) dropwise at room temperature and the resulting solution was stirred for 1 h, and 25 ml of 0.1 N AcOH was added to the resulting dark red solution. The aqueous layer was extracted with ether. The resulting organic layer was dried over MgSO₄. Solvents were removed under a reduced pressure, and the purification of the residue by Chromatotron chromatography gave 0.14 g (0.96 mmol, 48%) of *trans*-4-phenyl-3-buten-2-one. TLC (20% Ethyl acetate/*n*-hexane) *R_f* 0.42 IR (neat) 1668, 1608 cm^{-1} . NMR (CDCl₃) δ 7.42 (d, *J*=16.0 Hz, 1H), 7.40 (m, 5H), 6.65 (d, 1H, *J*=16.3 Hz), 2.30 (s, 3H). GC-MS 146 (M, 45), 131 (M-Me, 82), 103 (PhCHCH, 100), 77 (C₆H₅, 57), 43 (COCH₃, 25).

Reaction of Phenylacetylene with (3) and Alkyl Halides, A General Procedure. To a solution of disodium pentacarbonylchromate dianion (8 mmol) an alkyl halide (8.2 mmol) were added through a septum *via* a syringe at ambient temperature and the solution of mixture was stirred for 1 h. To this was added phenylacetylene (2 mmol) by a syringe at ambient temperature. After 1-2 h, a THF solution of NMMO (method A) or PPh₃ (method B) was added

through septum by a double ended needle. The resulting solution was stirred for 1 h and then poured into 50 ml of AcOH (0.1 N). The aqueous layer was extracted with ether and dried with MgSO₄. The solvents were removed under a reduced pressure, and the residue was purified by flash chromatography with elution first with hexane to remove naphthalene. Further elution with 10% ethyl acetate/*n*-hexane gave the desired *trans*-enones. *trans*- and *cis*-isomers were determined by the analysis of GC and ¹H-NMR. Physical data are given below.

4-Phenyl-3-buten-2-one. 74% (method A) and 89% (method B). TLC (20% Ethyl acetate/*n*-hexane) *R_f* 0.42. IR (neat) 1668, 1608 cm⁻¹. NMR (CDCl₃) δ 7.42 (d, *J*=16.0 Hz, 1H), 7.40 (m, 5H), 6.65 (d, *J*=16.3 Hz, 1H), 2.30 (s, 3H). GC-MS 146 (M⁺), 131, 103, 77, 43.

1-Phenyl-1-hexen-3-one. 51% (method A) and 72% (method B). TLC (10% Ethyl acetate/*n*-hexane) *R_f* 0.48. IR (neat) 1666, 1612 cm⁻¹. NMR (CDCl₃) δ 7.52 (d, *J*=16.2 Hz, 1H), 7.5 (m, 2H), 7.35 (m, 3H), 6.70 (d, *J*=16.5 Hz, 1H), 2.57 (t, *J*=7.4 Hz, 2H), 1.65 (m, *J*=7.4 Hz, 2H), 0.9 (t, *J*=7.5 Hz, 3H). GC-MS 174 (M⁺), 131, 103, 77, 41.

1-Phenyl-1-hepten-3-one. 75% (method A) and 88% (method B). TLC (20% Ethyl acetate/*n*-hexane) *R_f* 0.66. IR (neat) 1689, 1612 cm⁻¹. NMR (CDCl₃) δ 7.56 (d, *J*=16.2 Hz, 1H), 7.55 (m, 2H), 7.35 (m, 3H), 6.75 (d, *J*=16.3 Hz, 1H), 2.65 (t, *J*=7.4 Hz, 2H), 1.65 (m, *J*=7.3 Hz, 2H), 1.35 (m, *J*=7.5 Hz, 2H), 0.92 (t, *J*=7.3 Hz, 3H). GC-MS 188 (M⁺), 146, 131, 103, 77.

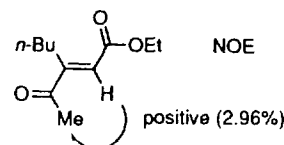
1-Phenyl-1-undecen-3-one. 44% (method A) and 71% (method B). TLC (20% Ethyl acetate/*n*-hexane) *R_f* 0.62. IR (neat) 1656, 1601 cm⁻¹. NMR (CDCl₃) δ 7.58 (d, *J*=16.4 Hz, 1H), 7.55 (m, 2H), 7.40 (m, 3H), 6.74 (d, 1H, *J*=16.3 Hz), 2.65 (t, 2H, *J*=7.6 Hz), 1.67 (m, 2H), 1.28 (m, 10H), 0.89 (t, 3H, *J*=6.4 Hz). GC-MS 244 (M⁺), 146, 131, 103, 77, 43, 41.

5-Methyl-1-phenyl-1-hexene-3-one. 7% (method A) and 46% (method B). TLC (10% Ethyl acetate/*n*-hexane) *R_f* 0.42. IR (neat) 1724, 1670 cm⁻¹. NMR (CDCl₃) δ 7.56 (d, *J*=16.4 Hz, 1H), 7.55 (m, 2H), 7.40 (m, 3H), 6.75 (d, *J*=16.1 Hz, 1H), 2.52 (d, *J*=7.0 Hz, 2H), 2.25 (m, *J*=6.8 Hz, 1H), 0.98 (d, *J*=6.6 Hz, 6H). GC-MS 188 (M⁺), 146, 131, 103, 77.

3-Tetradecen-2-one. 33% (method A), 47% (method B) and 22% yield (*t*-BuOO⁻Li⁺ as additive). TLC (10% Ethyl acetate/*n*-hexane) *R_f* 0.45. IR (neat) 1678, 1628 cm⁻¹. NMR (CDCl₃) δ 6.81 (m, *J*=16 Hz, *J*=6.9 Hz, 1H), 6.09 (m, *J*=15.9

Hz, *J*=1.6 Hz, 1H), 2.24 (s, 3H), 1.44 (m, 3H), 1.27 (m, 16H), 0.88 (t, *J*=6.5 Hz, 3H). GC-MS 210 (M⁺), 97, 71, 55, 43.

Ethyl *E*-2-acetyl-2-heptenoate. 10% (method A) and 32% (method B). TLC (10% Ethyl acetate/*n*-hexane) *R_f* 0.34. IR (neat) 1726, 1687, 1612 cm⁻¹. NMR (CDCl₃) δ 6.52 (s, 1H), 4.21 (q, *J*=6.9 Hz, 2H), 2.75 (m, *J*=6.9 Hz, 2H), 2.37 (s, 3H), 1.35 (m, 7H), 0.81 (t, *J*=6.0 Hz, 3H). GC-MS 198 (M⁺), 152, 110, 109, 81, 43.



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