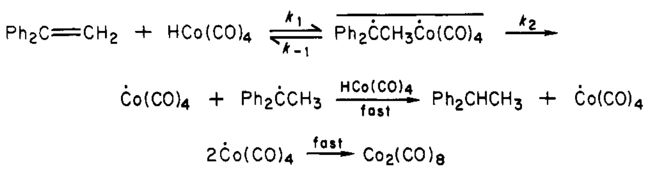
Scheme I



$$\mathrm{Ph_2C{=}CH_2 + HCo(CO)_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overline{Ph_2\dot{C}CH_3\dot{C}o(CO)_4} \xrightarrow{k_2}}$$

$$\mathrm{\dot{C}o(CO)_4 + Ph_2\dot{C}CH_3 \xrightarrow[fast]{HCo(CO)_4} Ph_2CHCH_3 + \dot{C}o(CO)_4}$$

$$\mathrm{2\dot{C}o(CO)_4 \xrightarrow{fast} Co_2(CO)_8}$$

It has been reported that when Ph_2CHBr is reacted with $Co_2(CO)_8$ in THF, $Ph_2CHCHPh_2$ is formed in good yield.[4] The THF disproportionates $Co_2(CO)_8$ to provide $[Co(CO)_4]^-$, and this anion reacts with the bromide to give $Ph_2\dot{C}H$ as an intermediate which couples to the observed dimer. When we repeated this experiment in the presence of $HCo(CO)_4$, Ph_2CH_2 was obtained in 95% yield. Apparently the radical intermediate abstracts hydrogen from $HCo(CO)_4$ faster than it dimerizes. Ph_2CHBr in THF reacts with $HCo(CO)_4$ in the absence of added $Co_2(CO)_8$ to give Ph_2CH_2, but the reaction is probably initiated by $[Co(CO)_4]^-$ available either from the strongly acidic[5] $HCo(CO)_4$ or from the disproportionation of $Co_2(CO)_8$ generated from the decomposition of $HCo(CO)_4$ in THF.[6]

The hydrogenation of α-methylstyrene with $HMn(CO)_5$, after which Scheme I is modeled, has also been reported to show a CIDNP effect.[7] The reported second-order rate law, inverse isotope effect, and deuterium exchange between reactants and products for $HMn(CO)_5$ reactions with α-methylstyrene are also characteristic of our reactions with $HCo(CO)_4$,[1] suggesting similar mechanisms for hydrogenations with $HMn(CO)_5$ and $HCo(CO)_4$.

$HCo(CO)_4$ was prepared as previously described.[1b] **$Ph_2C{=}CH_2$** was purchased from the Aldrich Chemical Co. **CIDNP** effects were observed on a Varian T 60-MHz ^1H NMR spectrophotometer.

CIDNP Effect with 1,1-Diphenylethylene. A 500-μL aliquot of freshly prepared 0.80 M (0.40 mmol) $HCo(CO)_4$ was injected into a NMR tube capped with a rubber septum and flushed well with CO. The NMR tube was then placed in a CO_2/acetone bath at −78 °C. The tube was then removed from the bath, and 40 μL (0.22 mmol) of 1,1-diphenylethylene was quickly injected into the $HCo(CO)_4$ solution. The NMR tube was then shaken vigorously for 2 s, wiped clean, and immediately placed in the NMR cavity at 31 °C. The spectrum is quickly scanned in the methyl proton region in order to observe the transient emission spectrum. The elapsed time between the injection of the olefin and the beginning of the spectrum scan must be 15–25 s or only an absorption spectrum will be observed. The entire reaction is over in about 60 s.

Reaction of $HCo(CO)_4/Co(CO)_4^-$ with Bromodiphenylmethane. In a 200-ml round-bottom flask well flushed with CO was placed a 78-mL THF solution of 0.185 M (14.0 mmol) $HCo(CO)_4$. To the solution was added 2.4 g (4.9 mmol) of $Co_2(CO)_8$ followed by the addition of 1.2 g (4.9 mmol) of bromodiphenylmethane dissolved in 5 mL of THF. The solution was stirred for 12 h at room temperature. The solvent was then evaporated and the residue redissolved in 70 mL of CH_2Cl_2. To this solution was then added dropwise 5 mL of ethylenediamine. The solution was then washed with H_2O, 2% aqueous HCl, and saturated aqueous NaCl before drying over $CaCl_2$ and filtering. Evaporation of the solvent gave a clear oil, 0.78 g (95% yield). Analysis by ^1H NMR showed it to be essentially pure diphenylmethane. ^1H NMR ($CDCl_3$): δ 7.1 (s, 10, phenyls), 3.9 (s, 2, methylene). When the above reaction was repeated in the absence of added $Co_2(CO)_8$, an 80% yield of Ph_2CH_2 was obtained; no coupled product could be detected (^1H NMR).

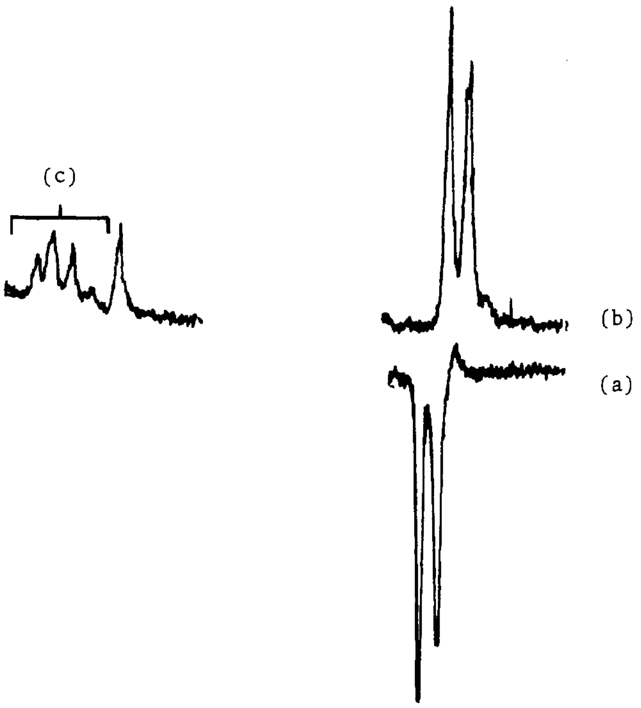


Figure 1. ^1H NMR spectra: (a) emission spectrum of Ph_2CHCH_3; (b) absorption spectrum of Ph_2CHCH_3 observed 20 s after a; (c) spectrum of Ph_2CHCH_3 with spinning side band of CH_2Cl_2.

Registry No. $HCo(CO)_4$, 16842-03-8; $Co_2(CO)_8$, 10210-68-1; 1,1-diphenylethylene, 530-48-3; bromodiphenylmethane, 776-74-9.

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[4] D. Seyferth and M. D. Miller, *J. Organomet. Chem.*, **38**, 373 (1972).

[5] T. E. Nalesnik and M. Orchin, *J. Organomet. Chem.*, **212**, C16 (1981).

[6] M. V. McCabe, J. F. Terrapane, and M. Orchin, *Ind. Eng. Chem. Prod. Res. Dev.*, **14**, 281 (1975).

[7] R. L. Sweany and J. Halpern, *J. Am. Chem. Soc.*, **99**, 8335 (1977).

Intermetallic Chalcogenide Atom Transfer and the Synthesis of 1,4-$[(CH_3C_5H_4)_2Ti]_2S_4$

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Received September 1, 1981

Summary: $(C_5H_4R)_2TiE_5$ (R = H, CH_3; E = S, Se) efficiently transfer a dichalcogenide fragment to $[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$ affording $Ir^{III}E_2$ complexes and in one case 1,4-$[(C_5H_4CH_3)_2Ti]_2S_4$. The unique Ti_2S_4 heterocycle can also be prepared via the PBu_3 desulfurization of $(C_5H_4CH_3)_2TiS_5$.

This report describes a new intermetallic atom transfer reaction[1] and the synthesis of a very unusual organotransition metal chalcogenide. The key reagents employed in this study are the dicyclopentadienyltitanium(IV) pentachalcogenides whose structures are composed of metallapentachalogenide rings.[2] The reactivity of these

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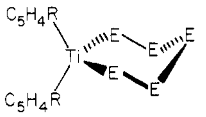
[1] For other examples of intermetallic atom transfer reactions see: Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248–1253. Reynolds, J. G.; Holm, R. H. *Inorg. Chem.* **1981**, *20*, 1873–1878.

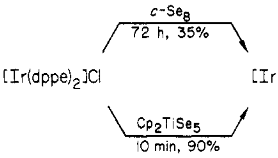
[2] Epstein, E. F.; Bernal, I. *J. Organomet. Chem.* **1971**, *26*, 229–245. Muller, K. G.; Petersen, J. L.; Dahl, L. F. *Ibid.* **1976**, *111*, 91–112.

compounds has been found to contrast sharply with that of the *cyclo*-octachalcogenides.[3]



1a, E = S, R = H
1b, E = S, R = CH_3
2a, E = Se, R = H
2b, E = Se, R = CH_3

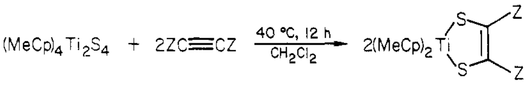
Equimolar quantities of **1a** or **1b** and $[Ir(dppe)_2]Cl$ (dppe = 1,2-bis(diphenylphosphino)ethane) **3**,[4] were found to react efficiently in dichloromethane solution (25 °C, 4 h). After solvent evaporation, washing with THF, and recrystallization of the residue from CH_2Cl_2–Et_2O, a 60% yield of orange, crystalline $[Ir(dppe)_2S_2]Cl$[5] was realized. The identity of this product was confirmed by detailed comparison of its 360-MHz ^1H NMR spectrum with that of the same compound prepared from **3** and c-S_8.[6] The efficient synthesis of $[Ir(dppe)_2Se_2]Cl$ by an analogous procedure from **2a** and **2b** is particularly notable since the published procedure[5] using c-Se_8 proceeds very sluggishly (eq 1). This result illustrates the utility of pentaselenides



(1)

2a and **2b** as conveniently reactive and soluble (8.3×10^{-3} and 1.0×10^{-2} M, respectively, in CH_2Cl_2 at 23 °C[7]) sources of elemental selenium. In contrast, c-Se_8 is practically insoluble in useful organic solvents ($<2.5 \times 10^{-5}$ M in CH_2Cl_2 at 23 °C[7]) wherein it reverts to the refractory, polymeric gray allotrope.

Chromatographic workup (CH_2Cl_2 elution on Merck PF 254 silica gel) of the products of the iridium desulfurization of **1b** afforded $(MeCp)_4Ti_2S_4$, **4b** ($R_f = 0.25$), a new compound isolated in 22% yield as red crystals from CH_2Cl_2–hexanes.[8] A symmetric structure with two S–S bonds was indicated for **4b** on the basis of its cleavage reaction with dimethyl acetylenedicarboxylate (eq 2). The



(64%) (2)

Z = CO_2CH_3

new dithiolene complex was purified by chromatography on Sephadex LH-20 (CH_2Cl_2 eluent) and can also be prepared directly from **1b**.[3] ^1H NMR spectroscopy indicates that **4b**, like its pentasulfido precursor, contains nonequivalent MeCp ligands (Figure 1). This observation is consistent with **4b** existing in a stereochemically rigid chair form.[2,9,10] Attempts to characterize the ring inversion by variable-temperature ^1H NMR spectroscopy were unsuccessful due to the thermal instability of this new compound. Compound **4b** is a unique example of a complex containing a cyclic M_2S_4 core and as such represents a new valence isomer of this topical chemical entity.[11,12]

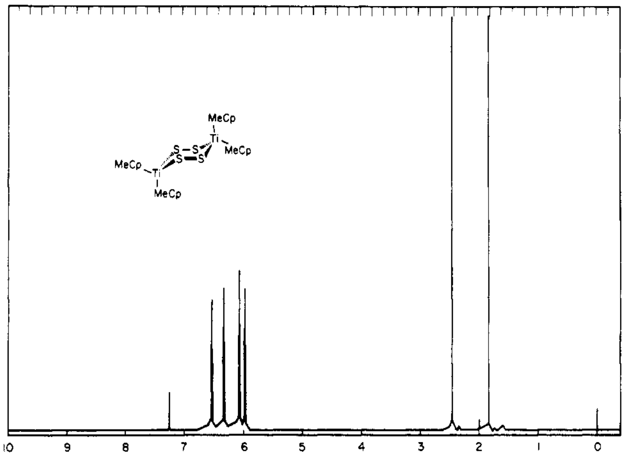


Figure 1. 360-MHz ^1H NMR spectrum of 1,4-$[(MeCp)_2Ti]_2S_4$ and its proposed structure.

The formation of **4b** via the iridium abstraction of an S_2 unit from **1b** would be expected to proceed via the intermediacy of $(MeCp)_2TiS_3$ which could couple to form the known dimer, 1,5-$[(MeCp)_2Ti]_2S_6$.[13] Curiously, we find that this cyclic *hexasulfide* is not readily desulfurized by **3**. Furthermore, 1,5-$[(MeCp)_2Ti]_2S_6$ was never detected in any reactions of **1b** with **3b**. However, we have found that the cyclic pentasulfide **1b** could be desulfurized to the cyclic tetrasulfide **4b** by using tri-n-butylphosphine. This discovery has led to an inexpensive, one-pot synthesis of **4b**. Treatment of **1b** with 3 equiv of $P(n\text{-}Bu)_3$ in refluxing CH_2Cl_2 for 15 min, followed by concentration and cooling to −20 °C, afforded pure **4b** as red needles in 28% yield (eq 3).

$$2(MeCp)_2TiS_5 + 6PBu_3 \rightarrow 1,4\text{-}[(MeCp)_2Ti]_2S_4 + 6SPBu_3 \quad (3)$$

An additional facet of the chemistry of **4b** is that it is formally, although not preparatively, the oxidized dimer of the dithiol, $(MeCp)_2Ti(SH)_2$[14] (eq 4). This interconversion represents a theme of continuing interest to us and others.[16]

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(3) A paper describing the detailed mechanistic and structural study of the reaction of the acetylenes with these titanium pentachalcogenides is in preparation.

(4) Vaska, L.; Catone, D. L. *J. Am. Chem. Soc.* **1966**, *88*, 5324–5325.

(5) Ginsberg, A. P.; Lindsell, W. E. *J. Chem. Soc. D* **1971**, 232–233. Bonds, W. D., Jr.; Ibers, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 3413–3419.

(6) Ginsberg, A. P.; Lindsell, W. E. *Inorg. Chem.* **1973**, *12*, 1983–1985.

(7) The solubilities were determined by UV–VIS spectrophotometry.

(8) Anal. Calcd for $C_{12}H_{14}S_2Ti$: C, 53.33; H, 5.22; Ti, 17.72. Found: C, 53.51; H, 5.22; Ti, 17.57. ^1H NMR ($CDCl_3$, 360 MHz): δ 6.54 (4 H, m, C_5H_4), 6.33 (4 H, m, C_5H_4), 6.07 (4 H, m, C_5H_4), 5.98 (4 H, m, C_5H_4), 2.46 (6 H, s, CH_3), 1.84 (6 H, s, CH_3). Field desorption mass spectrum: m/e 541 (M^+). IR (mineral oil mull): 1035, 939, 896, 870, 818, 422, 390 cm^{-1}. The corresponding products derived from **1a**, **2a**, and **2b** were insufficiently soluble to be purified.

(9) Köpf, H.; Block, B.; Schmidt, M. *Chem. Ber.* **1968**, *101*, 272–276.

(10) For a discussion of the conformational analysis of organic polysulfides, see: Allinger, N. L.; Hickey, M. J.; Kao, J. *J. Am. Chem. Soc.* **1976**, *89*, 2741–2745.

(11) For a synopsis of transition metal–S_2 complexes, see: Müller, A.; Jaegermann, W. *Inorg. Chem.* **1979**, *18*, 2631–2633.

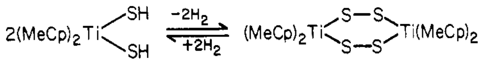
(12) Recent examples of metal complexes containing the M_2S_4 core: DuBois, D. L.; Miller, W. K.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1981**, *103*, 3429–3436. Clegg, W.; Christov, G.; Garner, C. D.; Sheldrick, G. M. *Inorg. Chem.* **1981**, *20*, 1562–1566. Müller, A.; Krickemeyer, E.; Reinsch, U. *Z. Anorg. Allg. Chem.* **1980**, *470*, 35–38. Chanaud, H.; Ducourant, A. M.; Giannotti, C. *J. Organomet. Chem.* **1980**, *190*, 201–216. Kubas, G.; Vergamini, P. J. *Inorg. Chem.* **1981**, *20*, 2667–2676.

(13) Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 5620–5621.

(14) This compound, prepared by using the method of McCall and Shaver[15] for the C_5H_5 derivative, is considerably easier to isolate in crystalline form. Anal. Calcd for $C_{12}H_{16}S_2Ti$: C, 52.93; H, 5.92; Ti, 17.58. Found: C, 52.85; H, 5.81; Ti, 17.51. ^1H NMR ($CDCl_3$, 90 mHz): δ (4 H, m, C_5H_4), 5.95 (4 H, m, C_5H_4), 3.09 (2 H, s, SH), 2.35 (6 H, s, CH_3). IR (mineral oil mull): 3079, 2562, 2545, 1083, 942, 921, 842, 815 cm^{-1}.

(15) McCall, J. M.; Shaver, A. *J. Organomet. Chem.* **1980**, *193*, C37–C39.

(16) For recent discussions of metallothiol–metallodisulfide interconversions see: Seyferth, D.; Henderson, R. S. *J. Organomet. Chem.* **1981**, *204*, 333–343. Küllmer, V.; Röttinger, E.; Vahrenkamp, H. *J. Chem. Soc., Chem. Commun.* **1977**, 782–783. Ramsani, T.; Taylor, R. S.; Sykes, A. G. *Ibid.* **1976**, 383–384.



$$2(MeCp)_2Ti(SH)_2 \underset{+2H_2}{\overset{-2H_2}{\rightleftharpoons}} (MeCp)_2Ti(S{-}S)_2Ti(MeCp)_2 \qquad (4)$$

Acknowledgment. This research was supported by the National Science Foundation and the Research Corp. Field desorption mass spectrometry facilities are supported by the National Cancer Institute. High-field NMR facilities were provided by the National Science Foundation (NSF Grant CHE 79-16100).

Registry No. 1a, 12300-91-3; **1b**, 78614-86-5; **2a**, 12307-22-1; **2b**, 78614-88-7; **3**, 15390-38-2; **4b**, 79816-62-9; $[Ir(dppe)_2S_2]Cl$, 40603-50-7; $[Ir(dppe)_2Se_2]Cl$, 40603-51-8; $(MeCp)_2Ti(SH)_2$, 79816-63-0; $P(n\text{-}Bu)_3$, 998-40-3.

Racemization of Chiral Tetrahedral Organotransition-Metal Clusters: A Novel Fluxional Process

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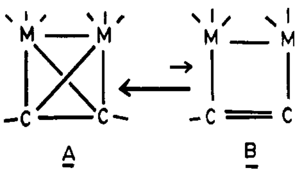
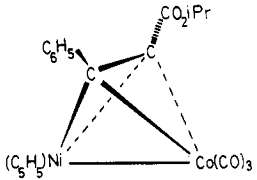
Summary: The intrinsically chiral tetrahedral organotransition-metal clusters $PhC{\equiv}CCO_2CHMe_2[(C_5H_5)Ni{-}M]$, where M is $Co(CO)_3$ (**1**), $(C_5H_5)Mo(CO)_2$ (**2**), or $Mn(CO)_4$ (**3**), have been prepared. The low symmetry of these molecules allows the detection and analysis of a new fluxional process, viz., the formal rotation of the M—M and C—C bond vectors. Using high-field NMR spectroscopy, $\Delta G^{\ddagger}$ for **2** is 20.5 ± 0.5 kcal/mol. The fluxionality and high reactivity of these molecules toward addition of an $Fe(CO)_3$ moiety are rationalized in terms of Wade's rules for electron-deficient clusters.

While many of the recent advances in cluster chemistry[1] have focussed on larger and larger molecular assemblies, the oldest and most widely investigated systems[2] still pose fascinating challenges not only of synthesis but also of bonding and molecular dynamics. Thus, to rationalize the high reactivity of the acetylene clusters A such as $\mu\text{-}(\eta^2\text{-}R_2C_2)Co_2(CO)_6$, it was suggested more than a decade ago[3] that they might be in equilibrium with the isomeric 1,2-dimetallacyclobutenes B (Scheme I). Although some extremely interesting observations have been reported,[4] there has been, to our knowledge, no unequivocal demonstration of a process corresponding formally to relative rotation of the C–C and M–M bond vectors in a tetrahedral cluster. Furthermore, calculations suggest that, for such an interconversion process to occur, a relatively high barrier must be surmounted.[5] We now report the construction of molecules possessing appropriate functionalities to allow us to probe the viability of such a process.

Scheme I



We have found that the reaction of $Co_2(CO)_8$, $(C_5H_5)_2Ni$ and an alkyne yields (inter alia) molecules of the type $(C_5H_5)NiCo(CO)_3(RC{\equiv}CR)$.[6] Similarly, the new mixed dimetallic series $(C_5H_5)NiMo(CO)_2(C_5H_5)(RC{\equiv}CR)$ is readily accessible by treatment of an alkyne with $(C_5H_5)_2Ni$ and $(C_5H_5)_2Mo_2(CO)_6$.[8,9] When the precursor acetylene bears two different substituents, these molecules are chiral and the incorporation of an isopropyl moiety, as in $(C_5H_5)NiCo(CO)_3(PhC{\equiv}C{-}CO_2CHMe_2)$ (1) and $(C_5H_5)NiMo(CO)_2(C_5H_5)(PhC{\equiv}C{-}CO_2CHMe_2)$ (2) provides diastereotopic methyl groups with which to monitor the rate of racemization of the complex and thus unmask the hitherto hidden process. In the absence of exchange the isopropyl methyls exhibit a pair of doublets which only



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[†] Ecole Nationale Supérieure de Chimie.

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[§] McMaster University.

(1) For a recent review, see: "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley-Interscience: New York, 1980.

(2) See, for example: Pino, P.; Braca, G. In "Organic Syntheses via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, p 419.

(3) Iwashita, Y.; Tamura, F.; Wakmatsu, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1520–1523.

(4) (a) Dickson, R. S.; Pain, G. N. *J. Chem. Soc., Chem. Commun.* **1979**, 277–278. (b) Boag, N. M.; Green, M.; Stone, F. G. A. *Ibid.* **1980**, 1281–1282.

(5) Calculations on $Cp_2Ni_2(C_2H_2)$ yield a barrier of 20.7 kcal/mol; Hoffmann, R.; Hoffman, D., personal communication.

(6) $Co_2(CO)_8$ (1 g, 2.9 mmol), $(C_5H_5)_2Ni$ (1 g, 5.3 mmol), and $C_6H_5C_2CO_2CHMe_2$ (1 g, 5.3 mmol) were heated at 100 °C in heptane under N_2 for 6 h and gave rise to the heterobimetallic acetylene complex 1 [25% yield; oil, *m/z* 453.9756, calcd *m/z* 453.9761; ^1H NMR (80 MHz) δ 7.66, 7.35 (m, C_6H_5), 5.31 (s, C_5H_5), 1.29 (d, CH_3, J = 6.6 Hz) in CD_2Cl_2 at 22 °C; δ (in C_6D_6 at 22 °C) 1.13 (d, CH_3, J = 6.4 Hz); IR (neat liquid) ν_{CO} 2055 (s), 2000 (vs), 1700 (s) cm^{-1}] as the main product together with (inter alia) $Ni_2Cp_2(CO)_2$, $Co_2(CO)_6(PhC_2CO_2\text{-}i\text{-}Pr)$, $Ni_2Cp_2(PhC_2CO_2\text{-}i\text{-}Pr)$, and $Co_2(CO)_4(PhC_2CO_2\text{-}i\text{-}Pr)_3$. These products were easily separated by TLC on silica gel using petroleum ether/ether (9:1). An alternative but less direct mode of access to the mixed bimetallic complex $(\mu\text{-}C_6H_5C_2C_6H_5)[(CO)_3Co{-}Ni(\eta^5\text{-}C_5H_5)]$ has recently appeared involving the reaction of $(C_5H_5)_2Ni_2(PhC_2Ph)$ with $Co_2(CO)_8$ (24% yield). The X-ray structural determination shows the acetylene bonded perpendicularly to the metal–metal bond.[7]

(7) Freeland, B. H.; Hux, J. E.; Payne, N. C.; Tyers, K. G. *Inorg. Chem.* **1980**, *19*, 693–696.

(8) $(C_5H_5)_2Ni$ (1 g, 5.3 mmol), $(C_5H_5)_2Mo_2(CO)_6$ (1.3 g, 2.7 mmol), and $PhC_2CO_2\text{-}i\text{-}Pr$ (1 mL, 5.3 mmol) were heated at 105 °C in 35 mL toluene for 7 h under N_2. TLC as before afforded 1.19 g (40%) of **2** as a red-brown crystalline solid: mp 90–91 °C; *m/z* 529.9922, calcd 529.992 54; IR (heptane) ν_{CO} 2030 (w), 1978 (sh), 1968 (vs), 1930 (s), 1902 (m), 1857 (s), 1682 (m) cm^{-1}; ^1H NMR ($CDCl_3$ at 30 °C at 80 MHz) δ 7.54, 7.25 (m, Ph), 5.24 (s, Cp), 5.14 (s, Cp), 1.35 (d, CH_3, J = 6.4 Hz); (in C_6D_6 at 30 °C) δ 1.22, 1.17 (dd, CH_3, J = 6.1 Hz)] together with $Ni_2Cp_2(CO)_2$, $Ni_2Cp_2(PhC_2CO_2\text{-}i\text{-}Pr)$, and unreacted $Mo_2Cp_2(CO)_6$. Similarly, other heterobimetallic species are accessible (e.g., $(\mu\text{-}PhC_2CO_2\text{-}i\text{-}Pr)[(CO)_4MnNi(\eta^5\text{-}C_5H_5)$ (**3**), mp 128 °C, was obtained from $Mn_2(CO)_{10}$ and Cp_2Ni in 40% yield).

(9) The 1857-cm^{-1} band in **2** suggests the presence of a semibridging carbonyl as in $[CpMo(CO)_2]_2C_2R_2$: Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764.

0276-7333/82/2301-0225$01.25/0