

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and DEGUSSA AG for generous gifts of chemicals. We are also grateful to Drs. W. Buchner and D. Scheutzwow for NMR measurements and to Mrs. U. Neumann and R. Schedl for the elemental

analysis.

Registry No. 2, 85944-34-9; 3, 85930-99-0; 4, 83525-75-1; *t,a*-5c, 85955-25-5; *t,s*-5c, 85955-27-7; 6, 107798-31-2; 11, 107798-32-3; 12, 107798-33-4; 12-*d*₁, 107798-34-5; [RhCl(C₅H₁₄)₂]₂, 12279-09-3; (C₅H₅)RhH₂(P-*i*-Pr₃), 81423-55-4; NaC₅H₅, 4984-82-1.

Stepwise Synthesis of Heteronuclear Pt₂M and PdPtM Clusters (M = Cr, Mo, W)

Peter Thometzek and Helmut Werner*

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg, Germany

Received January 8, 1987

The dinuclear complex $(\mu\text{-C}_5\text{H}_5)(\mu\text{-2-MeC}_3\text{H}_4)\text{Pt}_2(\text{P-}i\text{-Pr}_3)_2$ (1), which is prepared from $(\eta^5\text{-C}_5\text{H}_5)\text{Pt}(\eta^3\text{-2-MeC}_3\text{H}_4)$ and $\text{Pt}(\text{P-}i\text{-Pr}_3)_2$, reacts with Me_3SiBr to produce the structurally related compound $(\mu\text{-2-MeC}_3\text{H}_4)(\mu\text{-Br})\text{Pt}_2(\text{P-}i\text{-Pr}_3)_2$ (4). Reaction of 4 with $[(\text{C}_5\text{H}_5)\text{M}(\text{CO})_3]\text{Na}$ (M = Mo, W) leads to displacement of the bridging bromide by the tricarbonyl(cyclopentadienyl)metal anion and formation of the trinuclear clusters $(\text{C}_5\text{H}_5)(2\text{-MeC}_3\text{H}_4)(\text{CO})_3(\text{P-}i\text{-Pr}_3)_2\text{Pt}_2\text{M}$ (5, 6). The analogous mixed-metal PdPtM complexes 9-11 are similarly prepared, starting from $(\mu\text{-C}_5\text{H}_5)(\mu\text{-2-MeC}_3\text{H}_4)\text{PdPt}(\text{P-}i\text{-Pr}_3)_2$ (7) via $(\mu\text{-2-MeC}_3\text{H}_4)(\mu\text{-Br})\text{PdPt}(\text{P-}i\text{-Pr}_3)_2$ (8) as the intermediate that subsequently reacts with $[(\text{C}_5\text{H}_5)\text{M}(\text{CO})_3]\text{Na}$ (M = Cr, Mo, W) to form $(\text{C}_5\text{H}_5)(2\text{-MeC}_3\text{H}_4)(\text{CO})_3(\text{P-}i\text{-Pr}_3)_2\text{PdPtM}$ (9-11). The IR and ¹H, ¹³C, and ³¹P NMR spectroscopic data of 5, 6, and 9-11 confirm that the new heteronuclear clusters contain a tetrahedral Pt₂MC or PdPtMC framework, the carbon atom of which belongs to a triply bridging CO group.

Introduction

The chemistry of mixed-metal clusters is currently of high interest because of the unique reactivity patterns that are to be expected as a consequence of adjacent metals with different types of chemical properties.¹ Although some rational synthetic methods have recently become available,^{2,3} it still remains difficult to predict the exact composition of a heteronuclear metal-metal bonded product that could result from a given reaction. Therefore it is still a challenge to develop routes that produce cluster-type compounds in a *stepwise* fashion, providing *high yields* and avoiding the formation of side products with similar properties.

During the last 10 years we have shown that various dinuclear palladium and platinum complexes of general formula $(\mu\text{-X})(\mu\text{-Y})\text{M}_2(\text{PR}_3)_2$ (M = Pd, Pt) can be prepared by a route which we designated as "1 + 1 addition", that is by combination of two mononuclear starting materials, $\text{M}(\text{PR}_3)_2$ and $(\text{X})\text{M}(\text{Y})$.⁴ Particularly for M = Pd, the bridging ligands X and Y can easily be displaced *without cleavage* of the M-M bond. Owing to this robust nature we tried to introduce not only "classical" bridging ligands such as chloride or acetate but also organometallic anions in the hope that this would provide a new entry into the field of mixed-metal clusters. We were highly encouraged by MO calculations from Hofmann,⁵ which led to the

prediction that carbonyl metal complexes such as $[\text{Co}(\text{CO})_4]^-$ or $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3]^-$ should be useful reagents for the desired purpose.

The first experiments using dinuclear palladium compounds $(\mu\text{-C}_5\text{H}_5)(\mu\text{-X})\text{Pd}_2(\text{PR}_3)_2$ and $(\mu\text{-2-MeC}_3\text{H}_4)(\mu\text{-X})\text{Pd}_2(\text{PR}_3)_2$ (X = Cl, Br, CH₃CO₂) as starting materials have confirmed the prediction.^{6,7} In this paper we describe an extension of our original work which proves that also complexes containing Pt-Pt and Pd-Pt bonds can be employed as precursors for the synthesis of new heteronuclear clusters. A short communication reporting some preliminary results has already appeared.⁸

Results and Discussion

The dinuclear complex $(\mu\text{-C}_5\text{H}_5)(\mu\text{-2-MeC}_3\text{H}_4)\text{Pt}_2(\text{P-}i\text{-Pr}_3)_2$ (1), which is prepared from $(\eta^5\text{-C}_5\text{H}_5)\text{Pt}(\eta^3\text{-2-MeC}_3\text{H}_4)$ and $\text{Pt}(\text{P-}i\text{-Pr}_3)_2$,⁹ reacts with $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3]\text{Na}$ not to produce a Pt₂Mo cluster but to give the mononuclear compound $(\eta^1\text{-C}_5\text{H}_5)\text{Pt}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{P-}i\text{-Pr}_3)$ (2).¹⁰ The attempt to displace the cyclopentadienyl bridge in 1 by acetate, which should provide a more reactive starting material, also failed because in the reaction of 1 with acetic acid (see Scheme I) only the formation of complex 3 was observed.

The five-membered-ring ligand in 1 can be displaced, however, by bromide with Me₃SiBr as a reagent. By this

(1) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* 1980, 18, 207.

(2) Vahrenkamp, H. *Adv. Organomet. Chem.* 1983, 22, 169.

(3) Stone, F. G. A. *Angew. Chem.* 1984, 96, 85; *Angew. Chem., Int. Ed. Engl.* 1984, 23, 89.

(4) Werner, H. *Adv. Organomet. Chem.* 1981, 19, 155.

(5) Hofmann, P. Abstracts of Papers, Chemiedozententagung Kaiserslautern, 1982; p 113.

(6) (a) Werner, H.; Kraus, H.-J.; Thometzek, P. *Chem. Ber.* 1982, 115, 2914. (b) Werner, H.; Thometzek, P. *Angew. Chem.* 1982, 94, 707; *Angew. Chem., Int. Ed. Engl.* 1982, 21, 692.

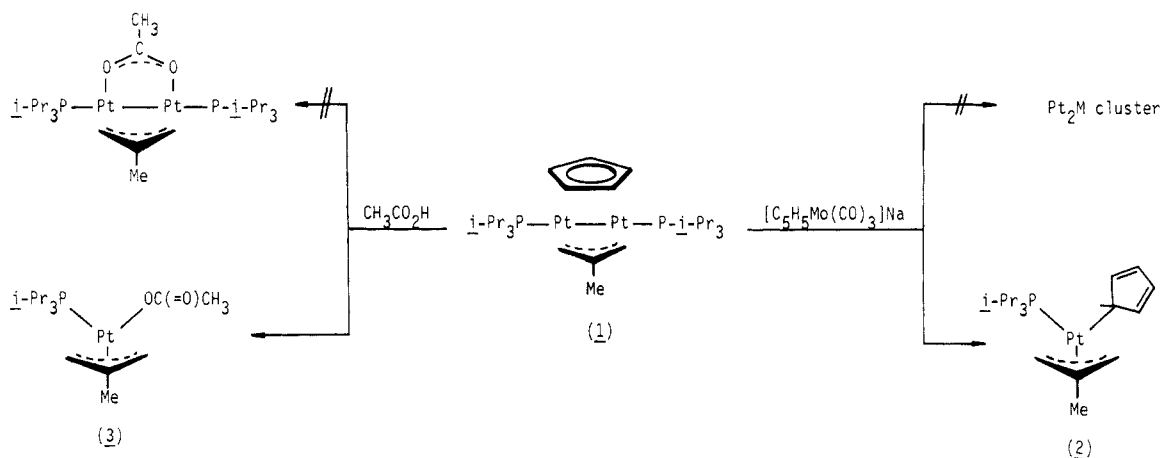
(7) Werner, H.; Thometzek, P.; Krüger, C.; Kraus, H.-J. *Chem. Ber.* 1986, 119, 2777.

(8) Thometzek, P.; Werner, H. *J. Organomet. Chem.* 1983, 252, C29.

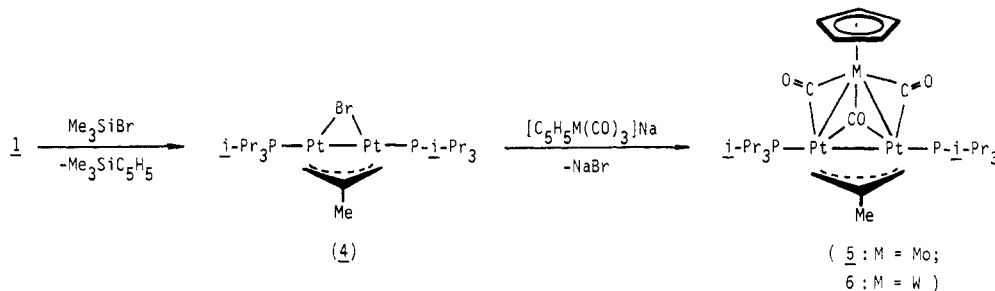
(9) Kühn, A.; Werner, H. *J. Organomet. Chem.* 1979, 179, 421.

(10) Werner, H.; Kühn, A.; Burschka, Ch. *Chem. Ber.* 1980, 113, 2291.

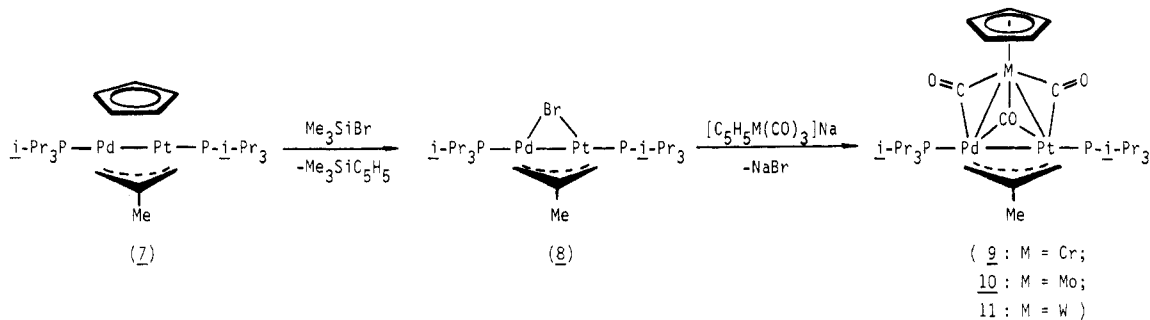
Scheme I



Scheme II



Scheme III



route, compound 4 is obtained in virtually quantitative yield. Similar to its palladium counterpart, (μ -2-MeC₃H₄)(μ -Br)Pd₂(P*i*-Pr₃)₂,⁴ it reacts with [C₅H₅]M(CO)₃Na (M = Mo, W) to produce the new heterotrinnuclear clusters 5 and 6. As a side product, the corresponding hydridometal complexes (C₅H₅)Mo(CO)₃H and (C₅H₅)W(CO)₃H also are formed, but these can be separated from 5 and 6 by column chromatography. We assume that in agreement with current concepts^{7,11} about the formation of Pd₂M₂ and Pd₂MM' clusters (M and M' = Cr, Mo, W) from [(C₅H₅)M(CO)₃]⁻ and mono- or dinuclear Pd₂ precursors, primarily an electron transfer from the tricarbonyl(cyclopentadienyl)metal anion to the Pt-containing substrate takes place. As a consequence, [(C₅H₅)M(CO)₃] radicals are formed which by hydrogen abstraction either from the solvent or the substrate produce the hydrido complex (C₅H₅)M(CO)₃H. 5 and 6, which are isolated in 54% and 65% yields, respectively, form red, only moderately air-sensitive crystals which similar to their Pd₂M analogues are easily soluble in most organic solvents, except for saturated hydrocarbons.

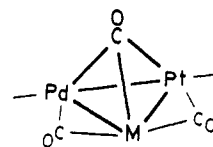


Figure 1. Cluster framework of 9–11.

The preparation of the PdPtM clusters 9–11 follows the same synthetic route used for 5 and 6. Displacement of the cyclopentadienyl bridge in (μ -C₅H₅)(μ -2-MeC₃H₄)-PdPt(P*i*-Pr₃)₂ (7) by bromide first gives (almost quantitatively) the dinuclear compound 8 (Scheme III) that on further reaction with [(C₅H₅)M(CO)₃]Na produces the trinuclear complexes 9–11 in 50–60% yield. As in the Pt₂ system, the synthesis of the PdPtM clusters is also accompanied by the formation of the hydridometal compounds (C₅H₅)M(CO)₃H that are separated from 9–11 by chromatographic techniques.

In contrast to the reaction of (μ -2-MeC₃H₄)(μ -X)Pd₂(P*i*-Pr₃)₂ (X = Cl, Br, CH₃CO₂) with Na[Co(CO)₄] that leads to the formation of a Pd₂Co cluster,⁷ treatment of 8 with the tetracarbonylcobalt anion under the same conditions does not produce the corresponding trinuclear PdPtCo complex. Instead, the Pd₂Co compound (2-MeC₃H₄)-

(11) Bender, R.; Braunstein, P.; Jud, J.-M.; Dusausoy, Y. *Inorg. Chem.* 1983, 22, 3394.

Table I. ¹H and ³¹P NMR Data of the Complexes 5, 6, and 9–11 in C₆D₆

	5	6	9	10	11
¹ H NMR ^a					
δ(C ₅ H ₅ M)	5.33 (s)	5.33 (s)	4.82 (s)	5.31 (s)	5.30 (s)
J(PtH)	4.1	5.0	3.7	4.3	3.3
δ(H _{syn})	b	b	3.66 (m)	3.83 (m)	3.92 (m)
δ(H _{anti})	b	b	2.08 (b s)	2.06 (b s)	2.26 (b s)
δ(CH ₃)	1.50 (t)	1.50 (t)	1.35 (dd)	1.37 (dd)	1.32 (dd)
J(PH)	3.0	3.5	3.1 ^c	2.9 ^c	2.9 ^c
δ(PCH)	2.30 (m)	2.32 (m)	2.14 (m)	2.12 (m)	2.12 (m)
δ(PCHCH ₃)	1.15 (dvt)	1.18 (dvt)	1.15 (dd), ^d 1.14 (dd) ^e	1.14 (dd), ^d 1.13 (dd) ^e	1.16 (dd), ^d 1.15 (dd) ^e
J(PH)/N	13.3	13.3	14.0, 13.7	13.0, 14.0	12.8, 13.8
J(HH)	7.0	7.0	6.7, 7.1	7.4, 6.9	7.0, 7.0
³¹ P NMR ^a					
δ(PdP)			29.8 (d)	29.5 (d)	26.9 (d)
δ(PtP)	35.0 (s)	35.0 (s)	43.3 (d)	43.6 (d)	46.2 (d)
J(PP)	92.3	80.0	110.2	113.1	111.6
¹ J(PtP)	4633	4653	4777	4761	4756
² J(PtP)	-116	-116	-81.9	-87.0	-95.3

^a¹H NMR: δ, Me₄Si internal standard. ³¹P NMR: δ, 85% H₃PO₄ external standard. J and N in Hz. Abbreviations used: s, singlet; d, doublet, t, triplet; m, multiplet, vt, virtual triplet; b, broad. ^bNot observed; decrease in intensity due to Pt–H coupling. ^cJ(¹PH) = J(²PH). ^dPR₃ on Pt. ^ePR₃ on Pd.

(CO)₄(P-*i*-Pr₃)₂CoPd₂ (12)⁷ is obtained in moderate yield. We assume that the first step following the attack of the [Co(CO)₄]⁻ anion on the starting material 8 consists in the cleavage of the Pd–Pt bond which is followed by recombination of the Pd-containing fragments with [Co(CO)₄]⁻ to form 12.

To the best of our knowledge, the new complexes 9–11 are the first heterometallic trinuclear clusters containing one palladium, one platinum, and one other transition metal in the cluster core. Owing to the spectroscopic data and the chemical properties, there is no doubt that their structure is completely analogous to that of the corresponding Pd₂M compounds.⁷ As is shown in Figure 1, the three metal atoms of 9–11 together with the carbon atom of one CO ligand form a tetrahedral framework of which two edges, Pd–M and Pt–M, are bridged by a carbonyl group. In accord with this structural proposal, the IR spectra show three strong CO stretching frequencies at ca. 1825, 1760, and 1710 cm⁻¹ that confirm the presence of doubly and triply bridging CO ligands. We assume that in solution an exchange between the carbonyl groups occurs because in the ¹³C NMR spectrum of 10 (in C₆D₆) at room temperature only one signal in the CO region (δ 229.2) is observed. Similar results have been obtained by Braunstein et al. in case of the tetranuclear clusters (C₅H₅)₂(CO)₆(PR₃)₂M₂M'₂ (M = Cr, Mo, W; M' = Pd, Pt)^{11,12} and also by us for the trinuclear complex (C₅H₅)₂(CO)₃(P-*i*-Pr₃)₂MoPd₂.^{6a} The appearance of only one NMR signal for the CO ligands can be rationalized insofar as owing to the structural data of the above-mentioned M₂M'₂ and MoPd₂ complexes, the bridging carbonyls are more tightly bound to the chromium, molybdenum, or tungsten atom than to the palladium or platinum atom.^{7,11,12}

The ¹H and ³¹P NMR data of 5, 6, and 9–11 are summarized in Table I. Due to the decrease in intensity caused by the ¹⁹⁵Pt satellites, in the ¹H NMR spectra of the Pt₂M complexes 5 and 6 besides the signals of the C₅H₅ and P-*i*-Pr₃ protons only the signal of the methyl protons of the 2-MeC₃H₄ ligand can be observed. The ¹H NMR spectra of the PdPtM compounds 9–11 show in addition to this signal also a multiplet at ca. δ 3.7–3.9 and a broad singlet at ca. δ 2.05–2.25 which are assigned to the H_{syn} and

H_{anti} protons of the allyl unit. The chemical shift as well as the splitting pattern of these signals are very similar to those of their Pd₂M analogues.⁷

The most characteristic feature of the ¹H NMR spectra of 9–11 certainly is the appearance of two PCHCH₃ signals of *unequal* intensity. This can be rationalized insofar as the signal of the phosphine ligand that is coordinated to platinum not only shows a H–H and P–H but also a Pt–H coupling. Therefore, this signal is less intense (by a factor of ca. 2/3) than the signal that belongs to the palladium-bound phosphine molecule.

The ³¹P NMR spectra of 9–11 are rather similar to the spectrum of 7.¹³ The two different ³¹P nuclei of the phosphine ligands couple with each other, and thus an AB-type pattern is observed. The P–P coupling constants are 110–113 Hz, i.e., significantly larger than in 7 (85 Hz) or in mononuclear bis(phosphine)platinum complexes.¹⁴ The presence of one ¹⁹⁵Pt atom in these molecules also induces a satellite spectrum which shows the AB part of an ABX spin system. In this satellite spectrum, two different Pt–P couplings are observed of which the larger one (ca. 4800–5200 Hz) is assigned to the ³¹P atom coordinated to platinum and the smaller one (ca. 82–95 Hz) to the ³¹P atom linked to palladium. The ³¹P NMR spectra of the Pt₂M complexes 5 and 6 show in addition to the singlet of the two equivalent phosphorus nuclei the expected satellites that in contrast to the spectra of 9–11 are symmetrically arranged with regard to the main peak. The Pt–P coupling constants derived from the satellite spectra are quite similar to those found for the PdPtM analogues.

Conclusion

The present study has confirmed that heteronuclear Pt₂M and PdPtM clusters containing a tetrahedral Pt₂MC or PdPtMC framework can be prepared in a stepwise manner from mononuclear starting materials. Similar to their Pd₂M counterparts, the new complexes 5, 6, and 9–11 also are members of the family of trinuclear 44-electron clusters having three metal–metal bonds. In a formal sense, the dicationic fragments [Pt₂(PR₃)₂]²⁺ and [PdPt(PR₃)₂]²⁺ are bridged by two anionic units, 2-MeC₃H₄⁻ and

(13) Werner, H.; Kühn, A. Z. Naturforsch., B: Anorg. Chem., Org. Chem. 1978, 33B, 1360.

(14) Finer, E. G.; Harris, R. K. Prog. Nucl. Magn. Reson. Spectrosc. 1971, 6, 61.

(12) Bender, R.; Braunstein, P.; Jud, J.-M.; Dusauroy, Y. Inorg. Chem. 1984, 23, 4489.

$[(C_5H_5)_3M(CO)_3]^-$, respectively, which behave as 4-electron donors and therefore create a 16-electron configuration on each platinum (or palladium) atom. Alternatively, the bonding in the Pt_3M and $PdPtM$ complexes can also be described by Wade's and Rudolph's rules.^{15,16} According to these, the three metal atoms in 5, 6, and 9–11 provide eight electrons (one from each Pd or Pt and six from M) for the cluster formation as it is necessary for a closo structure.

Experimental Section

NMR spectra were recorded on a Varian EM 360 L (1H), a Bruker WH 90 FT (^{31}P), and a Bruker Cryospec WM 400 (1H and ^{13}C) spectrometer and IR spectra on a Perkin-Elmer 457 spectrometer. The starting materials $(\mu-C_5H_5)_2(\mu-2-MeC_3H_4)Pt_2(P-i-Pr_3)_2$ (1) and $(\mu-C_5H_5)(\mu-2-MeC_3H_4)PdPt(P-i-Pr_3)_2$ (7) were prepared by published methods.^{9,13}

Reaction of 1 with $[(C_5H_5)_3Mo(CO)_3]Na$. A suspension of $[(C_5H_5)_3Mo(CO)_3]Na$ (16.0 mg, 0.06 mmol) in 0.5 mL of C_6D_6 was treated with 1 (50.0 mg, 0.06 mmol) and stirred for 24 h at room temperature. In the 1H and ^{31}P NMR spectra only the formation of the mononuclear complex $(\eta^3-C_5H_5)Pt(\eta^3-2-MeC_3H_4)(P-i-Pr_3)_2$ (2)¹⁰ could be observed.

Preparation of $(\eta^3-2-MeC_3H_4)Pt(P-i-Pr_3)OC(=O)CH_3$ (3). A solution of 1 (166 mg, 0.20 mmol) in 5 mL of toluene was treated at $-78^\circ C$ dropwise with acetic acid (11 μL , 0.20 mmol). Under vigorous stirring, the reaction mixture was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo and the residue recrystallized from toluene/pentane: yellow crystals; yield 115 mg (61%). Anal. Calcd for $C_{15}H_{21}O_2P_2Pt$: C, 38.38; H, 6.66; M_r , 469.48. Found: C, 38.74; H, 6.90; M_r , 440 (osmometric in benzene).

Preparation of $(\mu-2-MeC_3H_4)(\mu-Br)Pt_2(P-i-Pr_3)_2$ (4). A solution of 1 (415 mg, 0.50 mmol) in 10 mL of toluene was stirred at $-78^\circ C$ and treated dropwise with Me_3SiBr (66 μL , 0.50 mmol). After being stirred for 12 h at $-78^\circ C$, the solution was slowly warmed to room temperature and then filtered. The filtrate was concentrated in vacuo to ca. 1 mL and then treated with 10 mL of pentane. After the mixture was left standing at $-30^\circ C$, white crystals were formed which were filtered, washed with cold pentane, and dried in vacuo: yield 380 mg (91%); mp $78^\circ C$ dec; 1H NMR (C_6D_6) δ 2.25 (m, PCH), 1.73 (t, $J(PH) = 3.8$ Hz, allyl- CH_3); 1.14 (dvt, $N = 14.0$ Hz, $J(HH) = 6.8$ Hz, $PCHCH_3$); ^{31}P NMR (C_6D_6) δ 55.8 (s, $J(PP) = 41.7$ Hz, $^1J(PtP) = 5166$ Hz, $^2J(PtP) = -144$ Hz (coupling constants from the satellite spectrum)). Anal. Calcd for $C_{21}H_{49}BrP_2Pt_2$: C, 30.05; H, 5.78. Found: C, 30.27; H, 5.92.

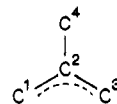
Preparation of $(C_5H_5)(2-MeC_3H_4)(CO)_3(P-i-Pr_3)_2MoPt_2$ (5). A solution of 4 (167 mg, 0.20 mmol) in 5 mL of toluene was treated at $-78^\circ C$ with small portions of $[(C_5H_5)_3Mo(CO)_3]Na$ (81 mg, 0.30 mmol). After being stirred for 2 h at $-78^\circ C$, the reaction mixture was slowly warmed to room temperature and stirred for 12 h. The solution was filtered, and the solvent was removed in vacuo. The residue was dissolved in 5 mL of toluene, and the solution was then chromatographed on silica gel. Elution with pentane gave a yellow band containing $C_5H_5Mo(CO)_3H$ (yield ca. 20–30%), and subsequent elution with toluene revealed a dark red band containing 5. The toluene solution was concentrated in vacuo to ca. 1 mL and then treated with 10 mL of pentane. After the mixture was left standing at $-30^\circ C$, brick red crystals were formed which were filtered, washed with cold pentane, and dried in vacuo: yield 110 mg (54%); mp $84^\circ C$ dec; IR (KBr) $\nu(CO)$ 1786, 1732 cm^{-1} . Anal. Calcd for $C_{30}H_{54}MoO_3P_2Pt_2$: C, 35.87; H, 5.70. Found: C, 35.64; H, 5.38.

Preparation of $(C_5H_5)(2-MeC_3H_4)(CO)_3(P-i-Pr_3)_2PtW$ (6). This complex was prepared analogously as described for 5, starting

with 4 (167 mg, 0.20 mmol) and $[(C_5H_5)_3W(CO)_3]Na$ (107 mg, 0.30 mmol): ruby red crystals; yield 143 mg (65%); mp $81^\circ C$ dec; IR (KBr) $\nu(CO)$ 1781, 1725 cm^{-1} . Anal. Calcd for $C_{30}H_{54}O_3P_2Pt_2W$: C, 32.89; H, 4.72; Pt, 35.65; W, 16.75. Found: C, 32.80; H, 4.95; Pt, 35.51; W, 16.73.

Preparation of $(\mu-2-MeC_3H_4)(\mu-Br)PdPt(P-i-Pr_3)_2$ (8). A solution of 7 (520 mg, 0.70 mmol) in 10 mL of toluene was stirred at $-78^\circ C$ and treated dropwise with Me_3SiBr (91 μL , 0.70 mmol). After being stirred for 2 h at $-78^\circ C$, the solution was slowly warmed to room temperature and worked up as described for 4: yellow-brown crystals; yield 495 mg (95%); mp $61^\circ C$ dec; 1H NMR (C_6D_6) δ 2.07 (m, PCH), 1.49 (dd, $J(^1PH) = J(^2PH) = 3.5$ Hz, allyl- CH_3); 1P is the phosphorus atom linked to Pt, 2P is the phosphorus atom linked to Pd), 1.14 (dd, $J(^1PH) = 14.0$ Hz, $J(HH) = 6.8$ Hz, $PCHCH_3$ from phosphine linked to Pt), 1.13 (dd, $J(^2PH) = 13.4$ Hz, $J(HH) = 7.0$ Hz, $PCHCH_3$ from phosphine linked to Pd); ^{31}P NMR (C_6D_6) δ 55.6 (d, $J(PP) = 64.0$ Hz, $^1J(PtP) = 5270$ Hz, $^2J(PtP) = -86.3$ Hz, PtP), 50.8 (d, $J(PP) = 64.0$ Hz, PdP). Anal. Calcd for $C_{21}H_{49}BrP_2PdPt$: C, 33.62; H, 6.74. Found: C, 33.87; H, 6.63.

Preparation of $(C_5H_5)(2-MeC_3H_4)(CO)_3(P-i-Pr_3)_2MPdPt$ (9–11). 9–11 were prepared analogously as described for 5, starting with 8 (250 mg, 0.34 mmol) and $[C_5H_5)_3M(CO)_3]Na$ ($M = Cr, Mo, W$; 0.50 mmol). 9: dark green crystals; yield 144 mg (48%); mp $52^\circ C$ dec; IR (KBr) $\nu(CO)$ 1820, 1754, 1710 cm^{-1} . Anal. Calcd for $C_{30}H_{54}CrO_3P_2PdPt$: C, 41.09; H, 6.20; Cr, 5.96. Found: C, 41.03; H, 6.20; Cr, 5.92. 10: ruby red crystals; yield 172 mg (55%); mp $61^\circ C$ dec; IR (KBr) $\nu(CO)$ 1826, 1756, 1710 cm^{-1} . ^{13}C NMR (C_6D_6) δ 229.2 (s, $J(PtC) = 118.0$ Hz, CO), 115.2 (s, C^2), 89.2 (s, C_5H_5), 52.6 (s, C^1, C^3), 30.8 (s, C^4), 26.1 (d, $J(PH) \approx 10$ Hz, PCH from phosphine linked to Pd), 25.7 (d, $J(PH) \approx 10$ Hz, PCH from phosphine linked to Pt), 20.4 (s, $PCHCH_3$ from phosphine linked to Pd); 19.9 (s, $PCHCH_3$ from phosphine linked to Pt). Assignment of the allylic carbon atoms:



Anal. Calcd for $C_{30}H_{54}MoO_3P_2PdPt$: C, 38.86; H, 6.04; Mo, 10.31; Pd, 11.30; Pt, 21.05. Found: C, 39.08; H, 5.90; Mo, 10.40; Pd, 11.54; Pt, 21.16. 11: dark red crystals; yield 203 mg (59%); mp $58^\circ C$ dec; IR (KBr) $\nu(CO)$ 1829, 1766, 1709 cm^{-1} . Anal. Calcd for $C_{30}H_{54}O_3P_2PdPtW$: C, 35.49; H, 5.31; W, 18.42. Found: C, 35.68; H, 5.39; W, 18.20.

Reaction of 8 with $[Co(CO)_4]Na$. A solution of 8 (170 mg, 0.23 mmol) in 5 mL of toluene was treated at $-78^\circ C$ with small portions of $[Co(CO)_4]Na$ (67 mg, 0.35 mmol). After being stirred for 1 h at $-78^\circ C$, the reaction mixture was slowly warmed to room temperature and stirred for 12 h. The solution was then filtered, the filtrate was concentrated in vacuo to ca. 1 mL, and 10 mL of pentane was added. After the mixture was left standing at $-30^\circ C$, yellow-brown crystals were formed which were characterized by IR and 1H NMR spectroscopy as $(2-MeC_3H_4)(CO)_4(P-i-Pr_3)_2CoPd_2$ (12),⁷ yield 61 mg (35%).

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and DEGUSSA AG (Hanau) for generous gifts of chemicals. We also thank Mrs. U. Neumann and Mrs. R. Schedl for the elemental analyses and Dr. W. Buchner and Dr. D. Scheutzw for NMR measurements.

Registry No. 1, 62586-35-0; 2, 74707-31-6; 3, 107799-25-7; 4, 88008-70-2; 5, 88008-69-9; 6, 88056-44-4; 7, 68993-55-5; 8, 87994-15-8; 9, 88008-66-6; 10, 88008-67-7; 11, 88008-68-8; 12, 83044-10-4; $[(C_5H_5)_3Mo(CO)_3]Na$, 12107-35-6; $(C_5H_5)_3Mo(CO)_3H$, 12176-06-6; $[(C_5H_5)_3W(CO)_3]Na$, 12107-36-7; $[Co(CO)_4]Na$, 14878-28-5; $[(C_5H_5)_3Cr(CO)_3]Na$, 12203-12-2; Pt, 7440-06-4; Mo, 7439-98-7; W, 7440-33-7; Co, 7440-48-4; Pd, 7440-05-3; $(C_5H_5)_3W(CO)_3H$, 12128-26-6.

(15) (a) Wade, K. *Chem. Br.* 1975, 11, 177. (b) Wade, K. *Adv. Inorg. Chem. Radiochem.* 1976, 18, 1.

(16) Rudolph, R. W. *Acc. Chem. Res.* 1976, 9, 446.