248 *Organometallics* **1999,** *18,* 248−257

Syntheses, Structures, and Reactivity of Dinuclear Molybdenum−Platinum and Tungsten−Platinum Complexes with Bridging Carbonyl, Sulfur Dioxide, Isonitrile, and Aminocarbyne Ligands and a dppa Backbone (dppa = $Ph_2PNHPPh_2$)

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Received September 9, 1998

The heterodinuclear *μ*-carbonyl complexes $[(OC)_4M(\mu\text{-}CO)(\mu\text{-dppa})Pt(PPh_3)]$ (**3a**, M = Mo; **3b**, M = W) are formed upon the reaction of $[(OC)_5M(\eta^1\text{-dppa})]$ (**1a**, M = Mo; **1b**, M = W) with $[Pt(C_2H_4)(PPh_3)_2]$. After addition of *p*-tosylmethyl isonitrile to **3**, the CO bridge is replaced by a bridging isonitrile ligand to afford $[(OC)_4W(\mu\text{-}C{=}NCH_2SO_2p\text{-tolyl})(\mu\text{-dppa})Pt(PPh_3)]$ (**4a**, M = Mo; **4b**, M = W). If stronger electron-donating isonitriles such as benzyl or 2,6-xylyl isonitrile are added to **3**, fragmentation into mononuclear complexes occurs. Protonation of **4** leads to the *μ*-aminocarbyne complexes $[(OC)_4M\{\mu\text{-}CN(H)CH_2SO_2p\text{-tolyl}\}(\mu\text{-dppa})Pt(PPh_3)][BF_4]$ (**5a**, M = Mo; **5b**, M = W), which react further with isonitriles to yield the *μ*-aminocarbyne complexes $[(OC)_3(RNC)W\{\mu\text{-}CN(H)CH_2SO_2p\text{-tolyl}\}(\mu\text{-dppa})Pt(PPh_3)][BF_4]$ **6**, (R = 2,6-xylyl, benzyl). Purging a solution of **4a** with SO_2 yields the complex $[(OC)_4Mo(\mu\text{-}SO_2)(\mu\text{-dppa})Pt(PPh_3)]$, **7a**, in which a triphenylphosphine oxide ligand is bound via a hydrogen bridge to the N−H group of the dppa backbone. X-ray diffraction studies performed on **4b** and **7a** reveal that the *μ*-CNR and the μ-SO_2 ligands bridge the metal centers in an asymmetric manner, the Pt−*μ*-C or Pt−*μ*-S distances being significantly shorter than the corresponding W−*μ*-C or Mo−*μ*-S distances, respectively.

Introduction

Despite the importance of isonitriles as ligands and substrates in organometallic and coordination chemistry, [1] studies concerning structure and reactivity of *heterobimetallics* M(*μ*-CNR)M′ possessing an isonitrile bridge between two *different* metal centers are still extremely scarce. The only representatives known so far are the A-frame complex $[C_6F_5Pd(\mu\text{-}C{=}Np\text{-tolyl})(\mu\text{-dppa})_2PtC_6F_5]$ and the structurally characterized Ni−Pt complex $[(MeCN)Ni(\mu\text{-}C{=}NMe)(\mu\text{-dppm})_2PtCl][Cl]$.[2] These two complexes resulted from formal insertion of CNR into the metal−metal bond of $[C_6F_5Pd(\mu\text{-dppa})_2PtC_6F_5]$ or were obtained by transmetalation reaction of $[(MeCN)Ni(\mu\text{-}C{=}NMe)(\mu\text{-dppm})_2Ni(CNMe)]$ with $[Pt(dppm)Cl_2]$.[2] In both cases, the *μ*-isonitrile ligand spans, as a two-electron donor, two metal centers of the same triad with a square planar coordination sphere. This paucity of heterobimetallic M(*μ*-CNR)M′ systems markedly contrasts the numerous examples of heterobimetallics and higher-nuclearity metal clusters reported in the literature possessing *terminal* isonitrile ligands. However, a bent or linear *μ*-CNR bonding mode is not uncommon in *homobimetallic* M(*μ*-CNR)M systems. The first complex of the bent type, $[(OC)CpFe(\mu\text{-}C{=}NPh)(\mu\text{-}CO)Fe(CO)Cp]$, has already been structurally characterized by Pauson et al. in 1965.[3a] In more recent papers the groups of Yamamoto and Mingos have shown that bridging isonitrile ligands in homobimetallic and cluster compounds may even adopt a nearly linear C=N−R arrangement.[3b−d]

We were therefore interested in *heterodinuclear* M(*μ*-CNR)M′ complexes containing metal centers possessing *different* coordination geometries and oxidation states in order to determine the steric and/or electronic effects governing the bonding mode (bridging vs terminal) of CNR ligands in heterometallic systems.[4] In the case of the bridging bonding mode some structural questions of interest concern (i) the angle C=N−R (linear **A** vs bent **B**), (ii) the relative orientation of the group R

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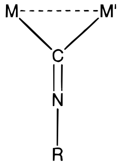
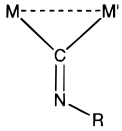
10.1021/om980756v CCC: $18.00

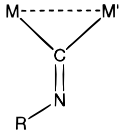
toward M or M′ for the bent case (**B** and **B′**), and iii) the position of the CNR bridge between the two metal centers (symmetric bonding mode **A**/**B** or asymmetric bridging bonding mode **C**).



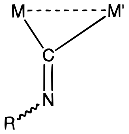
A



B



B'



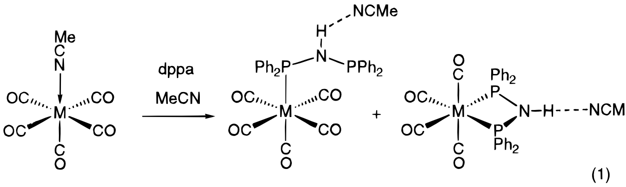
C

Apart from this structural aspect, our objective is to use the presence of two different metal centers for a bimetallic activation of the isonitrile ligand for further transformations such as carbon−carbon coupling reactions or conversion to μ-aminocarbyne ligands.

Since no structural information about bis(diphenylphosphino)amine-bridged heterobimetallic systems is available apart from our very recent studies on dinuclear dppa-bridged Fe−Pt systems,[4b] we have chosen this diphosphine ligand[5,6] to stabilize the metal−metal bond instead of the very common bis(diphenylphosphino)methane (dppm) ligand.[7] Recent comparative IR studies have established that dppa is somewhat less electron donating than dppm.[5d] We have shown that the selective substitution of the μ-CO ligand of [(OC)$_3$(Fe-(μ-CO)(μ-dppa)Pt(PPh$_3$)] by a CNR ligand offers a convenient access to complexes of the type [(OC)$_3$(Fe-(μ-C=NR)(μ-dppa)Pt(PPh$_3$)].[4b] With the aim to investigate heterobimetallic systems containing metal couples that are more separated in the periodic table than iron and platinum, we set out to prepare CO-bridged heterodinuclear Mo−Pt and W−Pt and to use them for the preparation of Mo(μ-CNR)Pt or W(μ-CNR)Pt complexes. In the context of our studies on heterobimetallics with bridging carbene, vinylidene, carbyne, and isonitrile ligands,[4,8] we report some results on the solid-state structures, synthesis, and reactivity of dppa-bridged Mo−Pt and W−Pt complexes with bridging isonitrile ligands.

Results and Discussion

Synthesis of the Metallophosphines [(OC)$_5$M(η^1-dppa)]. Metal complexes L$_n$M(η^1-R$_2$PXPR$_2$) containing a dangling diphosphine ligand are useful precursors for assembling polymetallic systems,[9] and numerous homo- and heterobimetallics have been prepared with bis(diphenylphosphino)methane.[7] We have already successfully employed [(OC)$_4$Fe(η^1-dppa)] as metallophosphine for the preparation of Fe−Pt and Fe−Re complexes.[4b,5c,d] It seemed therefore promising to employ related metallophosphines of the type [(OC)$_5$M(η^1-dppa)] (M = Mo, W) for the synthesis of dppa-bridged Mo−Pt and W−Pt compounds. Treatment of [(OC)$_5$M(NCMe)] with dppa in a 1:1 ratio afforded the metallophosphines **1** with a pendant dppa ligand (^{31}P{^{1}H} in CDCl$_3$ **1a**, δ 83.9 (d, P^1(Mo), ^2J(P^1−P^2) = 65 Hz), 32.9 (d, P^2); **1b**, 63.7 (d, P^1(W), ^2J(P^1−P^2) = 59 Hz, ^1J(P−W) 192 Hz), 32.7 (d, P^2)), together with the literature known chelate complexes **2**.[10,11] Whereas in the case of M = Mo only minor amounts of **2a** are formed (86% yield of **1a**), the isolation of pure **1b** (24%) was more difficult due to the formation of the chelate complex [(OC)$_4$W(dppa)] (**2b**) as the major species. Elemental analysis, ^{1}H NMR, and the X-ray diffraction studies (see below) indicate the coordination of one molecule of acetonitrile bound via a hydrogen bridge to the dppa ligand of **1** and **2**.



(1)

1a M = Mo
1b M = W

2a M = Mo
2b M = W

The X-ray structure determination of the metalloligand **1a** (Figure 1, Table 1) revealed that the overall geometry and bond lengths of the Mo(CO)$_5$P fragment are comparable to other complexes of the type [Mo-

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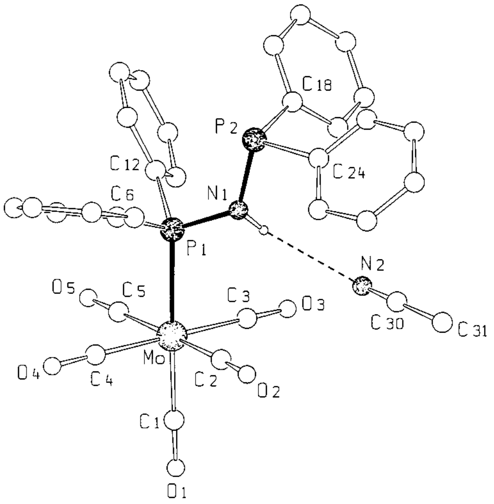


Figure 1. View of the crystal structure of $[(OC)_5Mo(dppa)]\cdot MeCN$ (**1a**) with the atom-numbering scheme.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 1a

Mo−P(1)	2.517(4)	P(1)−N(1)−P(2)	124.3(2)
Mo−C(1)	1.999(5)	N(1)−N(2)−C(30)	131.2(4)
Mo−C(2)	2.038(4)	P(1)−Mo−C(1)	178.3(1)
Mo−C(3)	2.038(4)	P(1)−Mo−C(4)	91.3(2)
Mo−C(4)	2.028(5)	P(1)−Mo−C(5)	90.2(2)
Mo−C(5)	2.033(4)	P(1)−Mo−C(3)	89.8(2)
P(1)−N(1)	1.682(3)	P(1)−Mo−C(2)	88.7(2)
P(2)−N(1)	1.718(4)	N(1)−P(1)−Mo	112.4(2)

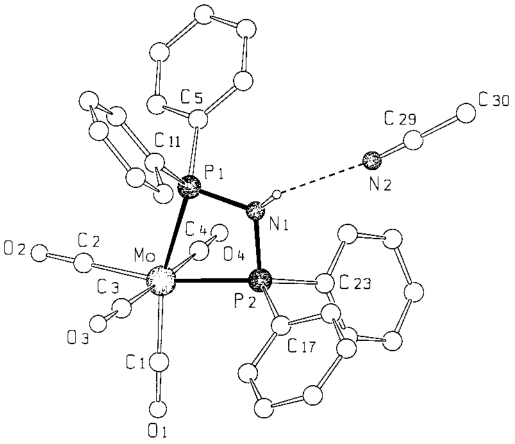


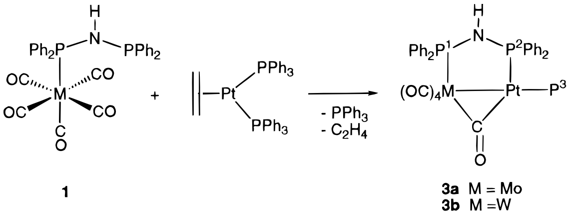
Figure 2. View of the crystal structure of $[(OC)_4Mo(dppa)]\cdot MeCN$ (**2a**) with the atom-numbering scheme.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 2a

Mo−P(1)	2.501(3)	P(1)−N(1)−P(2)	106.2(2)
Mo−P(2)	2.495(2)	P(1)−Mo−P(2)	65.29(6)
Mo−C(1)	1.989(4)	P(1)−Mo−C(1)	164.7(1)
Mo−C(2)	1.993(4)	P(2)−Mo−C(2)	169.0(1)
Mo−C(3)	2.013(5)	P(1)−Mo−C(2)	103.3(1)
Mo−C(4)	2.040(4)	P(2)−Mo−C(1)	99.6(1)
P(1)−N(1)	1.685(3)	N(1)−P(1)−Mo	94.2(1)
P(2)−N(1)	1.684(3)	N(1)−P(2)−Mo	94.4(1)

$(CO)_5PR_3]$.[12] The distance P(1)−N(1) of 1.682(3) Å is similiar to that reported for uncomplexed dppa (1.692(2) Å), whereas the distance P(2)−N(1) of 1.718(4) Å is somewhat elongated. The angle P(1)−N(1)−P(2) of 124.3(2)° is widened compared to that reported for the free ligand (118.9(2)°).[13] An acetonitrile molecule is weakly bound to the N−H group (*d*(N(1)−N(2)) 3.291(6) Å) of the dppa ligand. The presence of a hydrogen-bonded acetonitrile molecule (*d*(N(1)−N(2)) 3.088(5) Å) was also confirmed by an X-ray structure determination for the chelate complex **2a** (Figure 2). The bond lengths and angles of **2a** (Table 2) are very close to that reported for the chelate complex $[(OC)_4Mo(Ph_2PNEtPPh_2)]$.[14] Noteworthy is the very acute angle P(1)−Mo−P(2) of 65.29(6)°, thus bringing the two phosphorus atoms P(1) and P(2) in close contact with a separation of only 2.694(3) Å.

Synthesis of *μ*-CO-Bridged Heterobimetallics. Upon addition of $[Pt(C_2H_4)(PPh_3)_2]$ to a solution of **1a**,**b** in toluene, rapid evolution of ethylene occurred at ambient temperature, giving the yellow carbonyl-bridged $[(OC)_4M(\mu\text{-}CO)(\mu\text{-}dppe)Pt(PPh_3)]$ heterobimetallic complexes **3a**,**b** in more than 80% yield. Complexes **3** are air stable in the solid state for several hours, but begin slowly to decompose in solution after several hours at ambient temperature. They are highly soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$ and possess a moderate solubility in toluene, but are nearly insoluble in hexane and diethyl ether.



(2)

1

3a M = Mo
3b M =W

The proposed structure of the heterobimetallic compounds **3** in solution could be deduced from the combined NMR and IR data. The $^{31}P\{^1H\}$ NMR spectra of **3** display AMX patterns for the three mutually coupled phosphorus nuclei. The IR spectra of **3** in CH_2Cl_2 show three ν(CO) vibrations for the terminal carbonyls (**3a**, 2021 s, 1914 vs, br, 1890 sh; **3b**, 2018 s, 1908 vs, br) and a further vibration of medium intensity for the bridging carbonyl ligand (**3a**, 1805; **3b**, 1791 cm^{-1}). The solid-state IR spectrum of **3b** contains a sharp absorption band assigned to the N−H vibration (3318 cm^{-1}), which indicates the absence of hydrogen bonds as encountered in **1**.

Synthesis of *μ*-CNR-Bridged Heterobimetallics. Reaction of **3** with 1 equiv of *p*-tosylmethyl isonitrile led within 10 min to selective substitution of the bridging carbonyl to afford the yellow isonitrile-bridged complexes $[(OC)_4M(\mu\text{-}C{=}NCH_2SO_2p\text{-}tolyl)(\mu\text{-}dppa)Pt(PPh_3)]$ (**4a**, M = Mo; **4b**, M = W) according to Scheme 1. Although these *μ*-CNR complexes are stable for months in the solid state under a nitrogen atmosphere, they gradually decompose in solution after several hours, especially the Mo−Pt complex **4a**, which possesses a limited stability even at − 25 °C. Among the decomposition products, which have not been analyzed in detail, the chelates $[(OC)_4M(dppa)]$ are always found.

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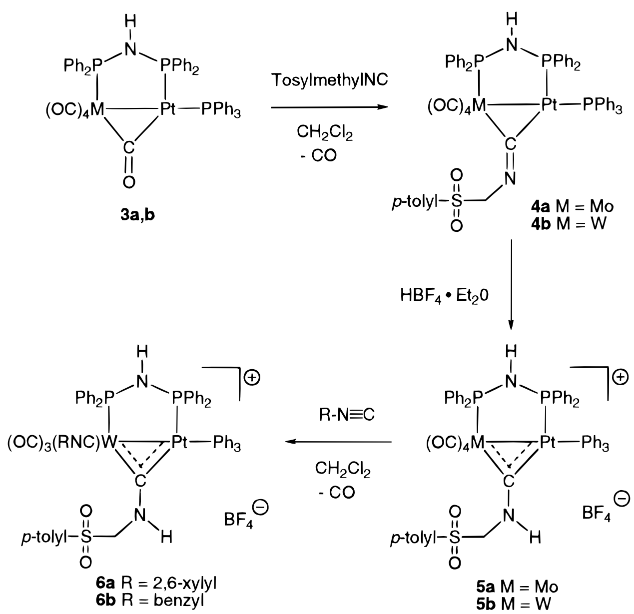
Scheme 1



Spectroscopic Studies. The NMR features of **4** resemble in general those of the precursors **3**. For instance, the $^{31}P\{^1H\}$ NMR spectrum of **4b** displays a doublet of doublets at δ 71.2 assigned to the platinum-bound dppa-phosphorus atom, which is strongly coupled ($^{2+3}J(P-P)$ = 134 Hz) with the tungsten-bound dppa phosphorus at δ 58.1. These signals are further split due to the presence of the PPh_3 ligand. The latter gives rise to a doublet of doublets at δ 43.7 with couplings of 39 and 56 Hz. All signals are flanked by ^{195}Pt satellites, whose Pt–P couplings are also found in the ^{195}Pt NMR spectrum (ddd at δ −2682 with $^1J(Pt-P)$ couplings of 4448 and 3253 Hz and a further $^{2+3}J(Pt-P)$ coupling of 49 Hz). Compared to the ^{31}P data of the μ-CO counterparts **3**, the following trends are noticeable: substitution of CO by CNR causes a lowering of the $^{2+3}J(P-P)$ coupling (166 Hz **3b** vs 134 Hz **4b**) and $^1J(Pt-P^2)$ coupling (3734 Hz vs 3253 Hz), whereas the $^1J(Pt-P^3)$ coupling (4199 Hz vs 4448 Hz) rises. The chemical shifts of the doublet of doublets of doublets resonances measured in the $^{195}Pt\{^1H\}$ NMR spectra of **3** and **4** are affected by neither the nature of the metal adjacent to the ^{195}Pt nucleus nor the C═Y bridge (Y = O, NR) and are found in the very narrow range between δ −2656 and −2682 ppm. The most significant change in the IR spectra of **4** is the replacement of the ν(CO) stretch of the bridging carbonyl of **3** against a broadened intense ν(C═N) stretch (**4a**: 1677; **4b**: 1669 cm^{-1}). These absorptions appear in the region typical for bridging isonitrile ligands; for example, the ν(C═N) stretch of corresponding Fe–Pt complex $[(OC)_3Fe(\mu\text{-}C{=}NCH_2SO_2p\text{-tolyl})(\mu\text{-dppa})Pt(PPh_3)]$ has been detected at 1648 cm^{-1}.[4b,c]

Despite our efforts, we could not succeed in isolating or characterizing even in solution by NMR spectroscopy any CNR derivatives with a CNR bridge analogous to **4** after stoichiometric addition of more nucleophilic isonitriles such as benzyl isonitrile or 2,6-xylyl isonitrile. IR monitoring revealed that immediately after isonitrile addition substitution of a terminal CO ligand occurs probably with formation of $[(OC)_3(RNC)M(\mu\text{-CO})(\mu\text{-dppa})Pt(PPh_3)]$. For example, 5 min after the addition of benzyl isonitrile to a CH_2Cl_2 solution of **3b** a broadened ν(C≡N) vibration of medium intensity, diagnostic for a terminal bound isonitrile ligand, has been observed at 2148 cm^{-1} besides three further ν(CO) stretches at 2018 (m), 1903 (vs, br), and 1792 (m) cm^{-1}. This heterobimetallic intermediate fragments within minutes to mononuclear species, so that attempts to obtain unambiguous evidence for the existence of $[(OC)_3(RNC)M(\mu\text{-CO})(\mu\text{-dppa})Pt(PPh_3)]$ by ^{31}P NMR monitoring remained unsuccessful. In a typical experiment using benzyl isonitrile, only several sets of doublets of doublets (δ 65.2 and 27.7, $J(P-P)$ = 26 Hz; δ 64.6 and 29.8, $J(P-P)$ = 44 Hz) have been detected together with the singlet resonance due to $[(OC)_4W(dppa)]$.[15] Note that in the case of the related dppm and dppa-bridged Fe–Pt complex $[(OC)_4(Fe(\mu\text{-CO})(\mu\text{-}Ph_2PXPPh_2)Pt(PPh_3)]$ with benzyl isonitrile or 2,6-xylyl isonitrile the stable μ-CNR complexes $[(OC)_3(Fe(\mu\text{-CNR})(\mu\text{-}Ph_2PXPPh_2)Pt(PPh_3)]$ (X = CH_2, NH) have been isolated as the sole products and structurally characterized by X-ray diffraction.[4b–d] We assume that in the case of the Mo–Pt and W–Pt systems no steric reasons are responsible for the lability of the isonitrile-substituted derivatives. It seems that predominantly the additional electron-donating influence of isonitriles, which are in general considered to be better σ-donors and weaker π-acceptors compared to a CO ligand, destabilizes these electron-rich heterobimetallic systems (three phosphorus donors and two metal centers in low oxidation states). Only in the case of p-tosylmethyl isonitrile possessing a strong electron-withdrawing SO_2-p-tolyl group does the π-acceptor capacity seem to be sufficient to prevent fragmentation. Theoretical calculations of Howell et al. on the bonding properties of isonitriles predict that the σ-donor character of isonitriles in a bridging bonding mode is comparable to that of linear terminal isonitrile ligands. However, the π-acceptor capacity strongly depends on the angle C═N–R and may even surpass that of carbon monoxide, if the degree of bending is significant enough.[16] This may explain why in the solid-state structure of **4b** a strong bending of 126.8° (see below) has been observed. Of course, the impact of packing effects may also influence the degree of the bending in the solid-state structure. Thus the combination of two factors—the electron withdrawing character of the CH_2SO_2p-tolyl group and its extreme bending—permits the p-tosylmethyl isonitrile ligand to compensate at least partially the electron-donating influence of the three phosphorus donors by back-bonding into its π^* orbitals. Further studies with other isonitriles possessing electron-withdrawing groups will show whether other stable complexes of the type $[(OC)_4M(\mu\text{-CNR})(\mu\text{-}Ph_2PXPPh_2)\text{-}Pt(PPh_3)]$ are accessible.

Crystal Structure of $[(OC)_4W(\mu\text{-}C{=}NCH_2SO_2p\text{-tolyl})(\mu\text{-dppa})Pt(Ph_3)]$ (4b). The proposed structure of **4b** (Figure 3, Table 3) in solution was also confirmed

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(15) (a) In the case of the reaction of $[(OC)_4W(\mu\text{-CO})(\mu\text{-dppm})Pt(PPh_3)]$ with benzyl isonitrile the isonitrile-substituted metallophosphine $[(OC)_4(BzNC)W(\eta^1\text{-dppm})]$ has been isolated. (b) Knorr, M. Unpublished results.

(16) (a) Howell, J. A. S.; Saillard, J.-Y.; Le Beuze, A.; Jaouen, G. *J. Chem. Soc., Dalton Trans.* **1982**, 2533. (b) The π-acceptor ability and bending of the μ-C═N–R moiety and the comparison with a μ-C═O group has also been investigated by means of Fenske–Hall calculations for complexes of the type $W_2(OH)_6(\mu\text{-CNR})$ and $W_2(OH)_6(\mu\text{-CO})$: Chisholm, M. H.; Clark, D. L.; Ho, D.; Huffman, J. C. *Organometallics* **1987**, *6*, 1532.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 4b

Pt−W	2.810(2)	Pt−C(1)−W	82.2(4)
Pt−C(1)	1.944(11)	C(1)−W−Pt	43.3(3)
Pt−P(3)	2.271(3)	C(1)−Pt−W	54.5(3)
Pt−P(2)	2.303(3)	C(1)−W−P(1)	105.3(3)
W−P(1)	2.498(3)	C(1)−Pt−P(2)	151.0(3)
W−C(1)	2.309(10)	C(1)−Pt−P(3)	97.9(3)
W−C(10)	1.97(2)	P(2)−Pt−P(3)	108.60(10)
W−C(11)	2.02(2)	W−Pt−P(3)	150.38(8)
W−C(12)	2.004(13)	W−Pt−P(2)	100.78(8)
W−C(13)	2.02(2)	Pt−W−P(1)	75.94(7)
C(1)−N(1)	1.229(12)	C(1)−W−C(13)	104.7(5)
C(2)−N(1)	1.436(13)	C(1)−W−C(12)	162.0(5)
C(2)−S	1.779(11)	C(1)−W−C(11)	84.9(5)
O(1)−S	1.439(8)	C(1)−W−C(10)	77.5(5)
O(2)−S	1.432(11)	C(13)−W−Pt	71.1(4)
P(1)−N(2)	1.703(9)	P(1)−W−C(10)	175.6(4)
P(2)−N(2)	1.688(10)	P(1)−W−C(13)	85.0(4)
P(1)−N(2)−P(2)	119.6(6)	P(1)−W−C(12)	89.6(4)
C(1)−N(1)−C(2)	126.8(10)	P(1)−W−C(11)	88.6(4)
N(1)−C(2)−S	110.8(8)	C(2)−S−C(3)	106.1(6)

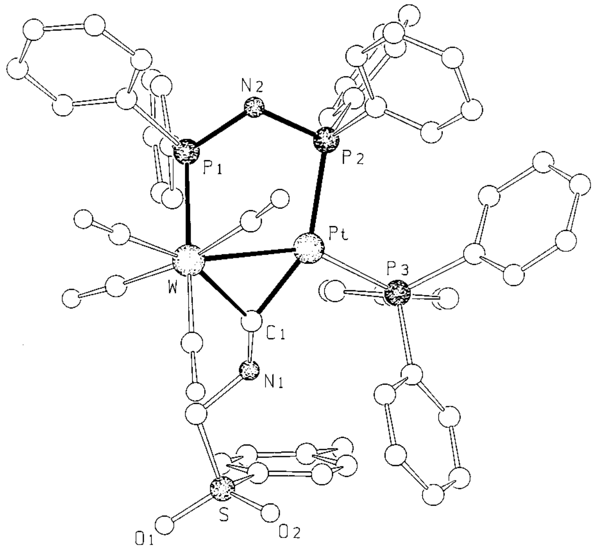

Figure 3. View of the crystal structure of [(OC)$_4$W(μ-CNCH$_2$SO$_2$$p$-tolyl)($\mu$-dppa)Pt(PPh$_3$)] (**4b**) with the atom-numbering scheme.

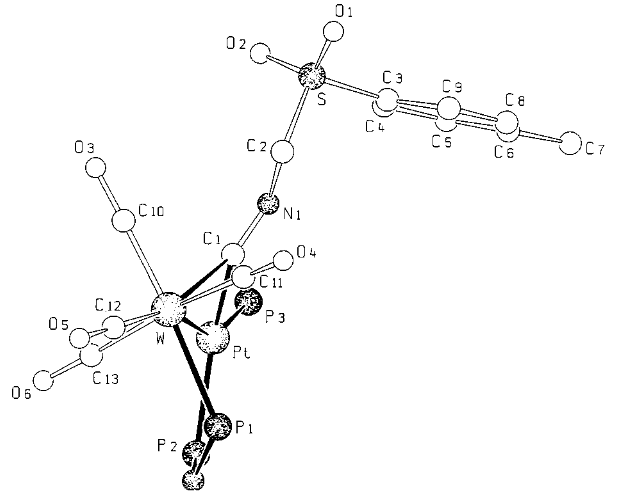

Figure 4. Perspective view of the core structure of **4b** along the W−Pt axis. The phenyl groups are omitted for clarity.

by a single-crystal X-ray diffraction study in the solid state. The W−Pt distance of 2.810(2) Å indicates a metal−metal bond and is close to the values found in other complexes of this type.[17] The tungsten and platinum atoms are linked by a dppa bridge. The bridging isonitrile ligand is extremely asymmetrically situated between the two metals with W−C(1) and Pt−C(1) distances of 2.309(10) and 1.944(11) Å, respectively. A very similar asymmetric arrangement has been encountered for Stone's carbene-bridged compounds [(OC)$_4$W(μ-C(OMe)p-tolyl)(μ-dppm)Pt(CO)] and [(OC)$_5$W(μ-C=CH$_2$)Pt(dppm)].[17a,b] For the former dppm-bridged complex, the asymmetry of the three-membered Pt{μ-C(OMe)p-tolyl}W ring [Pt−C 1.97(3), W−C 2.49(3) Å] is even more accentuated than in the case of **4b**. This asymmetry has been discussed in terms of a formal coordination of a R(MeO)C=PtL$_2$ moiety to a W(CO)$_4$-PR$_3$ fragment. The length of the C(1)−N(1) double bond of 1.229(12) Å is comparable to that reported for other isonitrile-bridged systems.[18] The C(1)−N(1)−C(2) angle is strongly bent (126.8(10)°) and aligned parallel to the Pt−W axis, with the tosylmethyl group oriented toward the tungsten center. This inclination exceeds the C−N−C angle of the μ-C=N-Me ligand of [(MeCN)Ni(μ-C=NMe)(μ-dppm)$_2$PtCl][Cl],[2b] which amounts to 132.3° (from Cambridge Data Base). We believe that this strong bending may have its origin in *electronic* reasons (see above); however, the orientation toward the carbonyl fragment is imposed by the *steric bulkiness* of the triphenyl phosphine ligand on platinum, which would otherwise interfere in a unfavorable manner with the p-tosylmethyl group. The coordination about the seven-coordinate tungsten atom is completed by four terminal CO ligands and may be viewed as distorted octahedral (when neglecting the metal−metal bond) and that of the Pt atom as distorted square planar. The rms deviation from the mean plane defined by Pt, W, P(2), P(3), and C(1) has been determined to be 0.169 Å. The mutual inclination of the two metal fragments, which is manifested in the torsion angle P(1)−W−Pt−P(2) of 31.6(1)° between the two dppa-phosphorus atoms, can be seen in Figure 4 showing the core structure of **4b** along the W−Pt axis.

Synthesis of Cationic μ-Aminocarbyne Complexes. We have recently shown that the addition of various electrophiles to the basic nitrogen of the isonitrile bridge of complexes of the type [(OC)$_3$Fe{μ-CNR}(μ-Ph$_2$PXPPh$_2$)Pt(PPh$_3$)] represents a convenient method for the preparation of heterobimetallics bridged by an aminocarbyne ligand, a class of compound that has been previously unknown.[4,19] To probe whether in the case

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[17] (a) Mead, K. A.; Moore, I.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2083. (b) Awang, M. R.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2091. (c)Awang, M. R.; Barr, R. D.; Green, M.; Howard, J. A. K.; Marder, T. B.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1985**, 2009. (d) Powell, J.; Sawyer, J. F.; Smith, S. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1312. (e) Lukehart, C. M.; True, W. R. *Organometallics* **1988**, *7*, 2387. (f) Braunstein, P.; Bellefon, C. D. M. D.; Oswald, B.; Ries, M.; Lanfranchi, M.; Tiripicchio, A. *Inorg. Chem.* **1993**, *32*, 1638.

[18] (a) Olmstead, M. M.; Hope, H.; Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1977**, *99*, 5502. (b) Busetto, L.; Carlucci, L.; Zanotti, V.; Albano, V. G.; Braga, D. *J. Chem. Soc., Dalton Trans.* **1990**, 243. (c) Wu, W.; Fanwick, P. E.; Walton, R. A. *Organometallics* **1997**, *16*, 1538. (d) Ruiz, J.; Riera, V.; Vivanco, M.; Garcia-Granda, S.; Pertierra, P. *Organometallics* **1992**, *11*, 2734. (e) DeLaet, D. L.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1986**, *5*, 1807.

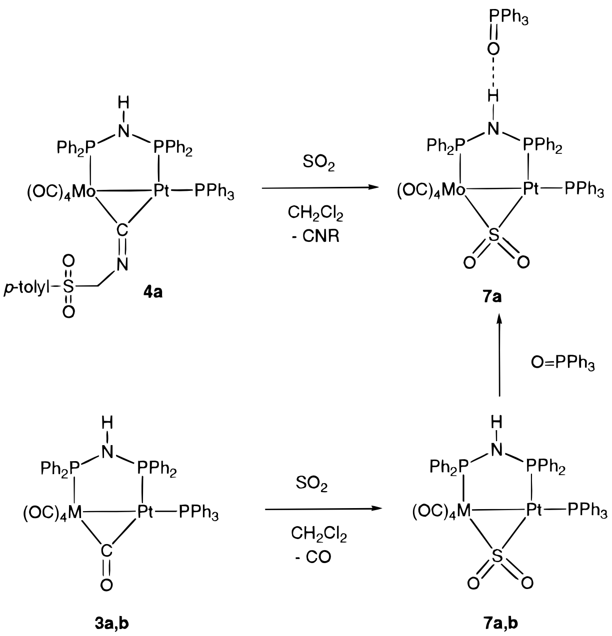
[19] A μ-CN(Et)Me-bridged W−Au aminocarbyne complex has been recently structurally described: Albano, V. G.; Busetto, L.; Cassani, M. C.; Sabatino, P.; Schmitz, A.; Zanotti, V. *J. Chem. Soc., Dalton Trans.* **1995**, 2087.

of **4** addition of H^+ occurs also on the isonitrile bridge or whether alternatively protonation of the metal−metal bond or the metal centers leading to hydride complexes is preferred, we reacted **4** with an excess of $HBF_4 \cdot Et_2O$ at 253 K. After addition of the latter to a solution of **4** in dichloromethane, instantaneous N-protonation occurs, leading exclusively to the yellow cationic μ-aminocarbyne complexes $[(OC)_4M\{\mu\text{-}CN(H)CH_2SO_2p\text{-tolyl}\}(\mu\text{-dppa})Pt(PPh_3)][BF_4]$, **5**. These complexes may alternatively be considered as dimetalated iminium salts, a formalism that has been employed by A. R. Manning et al. for the description of the bonding mode in the case of homodinuclear compounds of the type $[CpFe(CO)_2(\mu\text{-}CNRR')Fe(CO)_2Cp]^+$.[20] It seems that the stronger π-acceptor character of the μ-aminocarbyne ligand (compared to a μ-CNR ligand) in addition to the positive charge causes a significant stabilizing effect. Whereas the neutral bimetallics **3** and **4** (e.g., **4a**) gradually decompose in chlorinated solvents, the higher stability of **5** permitted now the recording of $^{13}C\{^1H\}$ NMR spectra. The resonance of the μ-carbyne carbon of **5b** was detected at δ 318.5 (dd, $^2J(P-C)$ = 9, 68 Hz), together with three sets of doublets for terminal carbonyl ligands at δ 195.2 (2 CO, $^2J(P-C)$ = 8 Hz), 197.5 (d, 1 CO, $^2J(P-C)$ = 15 Hz) and 199.3 (d, 1 CO, $^2J(P-C)$ = 9 Hz). A broad doublet at δ 75.3 ($^4J(P-C)$ = 15 Hz) was assigned to the NCH_2 carbon and a singlet at δ 21.6 to the methyl group of the tosyl group. In the ^{195}Pt NMR spectra of **5**, the protonation of the isonitrile bridge has a marked influence on the chemical shifts of the ddd resonances, which are shifted to ca. 290 ppm to lower field (**5a**, δ −2392; **5b**, δ −2385) compared to the precursors **4**.

Synthesis of Isonitrile-Substituted μ-Aminocarbyne Complexes. Stoichiometric addition of 2,6-xylyl isonitrile or benzyl isonitrile to **5b** leads to selective substitution of a carbonyl ligand to yield the stable μ-aminocarbyne complexes $[(OC)_3(RNC)W\{\mu\text{-}CN(H)CH_2SO_2p\text{-tolyl}\}(\mu\text{-dppa})Pt(PPh_3)][BF_4]$ (**6a**, R = 2,6-xylyl; **6b**, R = benzyl), which have also been fully characterized by elemental analysis, FAB$^+$ mass spectrometry, multinuclear NMR, and IR spectroscopies. In addition to the two carbonyl vibrations at 2018 (m) and 1938 (vs) cm^{-1}, a strong isonitrile absorption band is found at 2136 cm^{-1} in the IR spectrum of **6a**; a weak band at 1596 cm^{-1} is tentatively assigned to the ν(CN) band of the aminocarbyne ligand. In the $^{13}C\{^1H\}$ NMR of **6a** the μ-carbyne resonance at δ 314.7 (ddd, $^2J(P-C)$ = 3, 6, 66 Hz) is somewhat high-field shifted compared to that of **5b**. The observation of two carbonyl signals at δ 200.6 (d, 1 CO, $^2J(P-C)$ = 20 Hz) and δ 198.6 (dd, 2 CO, $^2J(P-C)$ = 2, 9 Hz), a broadened isonitrile resonance at δ 155.1 (d, $^2J(P-C)$ = 10 Hz) together with a broad doublet ($^4J(P-C)$ = 12 Hz) at δ 74.9, arising from the NCH_2 group, and two singlets at δ 21.6 and 18.2 in a 1:2 ratio further corroborate our structural proposal for **6a**.

Synthesis of Heterodinuclear μ-SO_2 Complexes. To see whether the bridging bonding mode of the μ-isonitrile ligand remains after addition of other ligands, which are known to behave as strong π-acceptors, we purged a dichloromethane solution of **4a** under a gentle stream of SO_2 for 5 min. IR monitoring of the reaction after 10 min revealed the complete disappearance of **4a** and the formation of several new complexes. We suggest the initial formation of a species of the type $[(OC)_3(CNCH_2SO_2p\text{-tolyl})Mo(\mu\text{-}SO_2)(\mu\text{-dppa})Pt(Ph_3)]$ having a terminal bound isonitrile ligand, since a ν(CN) stretch was observed at 2119 cm^{-1}. However, layering a concentrated solution of the reaction mixture with hexane afforded after 3 days in 44% yield orange crystals of the sulfur dioxide-bridged complex $[(OC)_4Mo(\mu\text{-}SO_2)(\mu\text{-dppa})Pt(PPh_3)] \cdot O{=}PPh_3$ **7a**, which has surprisingly lost the isonitrile ligand (Scheme 2). ^{31}P NMR spectroscopy, elemental analysis, and an X-ray diffraction study revealed (see below) that additionally a triphenylphosphine oxide molecule interacts via a hydrogen bridge with the N−H group of the dppa ligand. This may be explained by partial decomposition/oxidation during the crystallization. This complex was alternatively prepared in improved yields (79%) by reaction of the μ-CO complex **3a** with SO_2 under selective substitution of the bridging CO ligand (Scheme 2) and subsequent addition of a stoichiometric amount of $O{=}PPh_3$. For comparison, the W−Pt complex $[(OC)_4W(\mu\text{-}SO_2)(\mu\text{-dppa})Pt(PPh_3)]$, **7b** was prepared also in an analogous manner. Infrared monitoring of the course of the reaction showed quantitative conversion after 10 min under gentle SO_2 purge. Precipitation with hexane yielded **7b** as an analytically pure yellow powder, which remained unchanged even after exposure to air for several hours. We assign two vibrations of medium intensity at 1183 and 1044 cm^{-1} (KBr), absent in the IR spectrum of $[(OC)_4W(\mu\text{-}CO)(\mu\text{-dppa})Pt(PPh_3)]$, **3b**, to the ν(SO) frequencies of the bridging sulfur dioxide ligand. This region seems, according to previous studies of Kubas, to be very characteristic for a μ-SO_2 bonding mode.[21] For example, almost identical ν(SO) values (1186 and 1048 cm^{-1}) have

Scheme 2



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(20) (a) Willis, S.; Manning, A. R.; Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1980**, 186. (b) Cox, G.; Dowling, C.; Manning, A. R.; McArdle, P.; Cunningham, D. *J. Organomet. Chem.*, **1992**, *438*, 143.

(21) Kubas, G. J. *Inorg. Chem.* **1979**, *18*, 182.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 7a

Pt−Mo	2.9332(10)	S−Pt−Mo	56.82(4)
Pt−S	2.2000(12)	S−Mo−Pt	47.24(3)
Pt−P(3)	2.2904(13)	Pt−S−Mo	75.94(3)
Pt−P(2)	2.3167(14)	P(1)−Mo−S	111.24(5)
Mo−P(1)	2.502(14)	P(2)−Pt−S	152.98(4)
Mo−S	2.5308(17)	P(1)−Mo−Pt	75.27(4)
Mo−C(1)	2.039(6)	P(2)−Pt−Mo	97.40(4)
Mo−C(2)	2.007(5)	P(3)−Pt−Mo	158.13(3)
Mo−C(3)	2.016(6)	P(2)−Pt−P(3)	104.47(5)
Mo−C(4)	2.049(9)	S−Mo−C(1)	84.59(16)
S−O(5)	1.462(3)	S−Mo−C(2)	78.21(16)
S−O(6)	1.472(3)	S−Mo−C(3)	159.44(17)
O(1)−C(1)	1.141(6)	S−Mo−C(4)	102.13(16)
O(2)−C(2)	1.137(6)	P(1)−Mo−C(1)	87.01(15)
O(3)−C(3)	1.133(7)	P(1)−Mo−C(2)	170.44(15)
P(1)−N	1.684(4)	P(1)−Mo−C(3)	86.47(16)
P(2)−N	1.685(4)	P(1)−Mo−C(4)	88.79(15)
P(4)−O(7)	1.487(4)	P(1)−N−P(2)	119.5(2)

been reported for $[(OC)_2W(\mu\text{-}CO)(\mu\text{-}SO_2)(\mu\text{-dppm})_2RhCl]$.[22d,23a]

Crystal Structure of $[(OC)_4Mo(\mu\text{-}SO_2)(\mu\text{-dppa})Pt(PPh_3)]\cdot O{=}PPh_3$ (7a). Several examples of heterodinuclear μ-SO_2 complexes have been reported during the past decade. [22] However, only two of them have been crystallographically studied very recently. The two examples possessing a metal−metal bond are $[(OC)_2Mo(\mu\text{-}CO)(\mu\text{-}SO_2)(\mu\text{-dppm})_2RhCl]$ and $[Cp^*Ni(\mu\text{-}SO2)(\mu\text{-}CO)W(MeCp)]$ prepared by Lorenz's and Chetcuti's groups, respectively.[23] We therefore determined the structure of **7a** by an X-ray diffraction study. Suitable crystals of **7a** containing two molecules of CH_2Cl_2 and a hydrogen-bound $O{=}PPh_3$ molecule were obtained from a concentrated CH_2Cl_2 solution layered with hexane. The separation of the two metal centers (2.933(1) Å) (Table 4) is significantly longer compared to that of **4b**, but falls still in the range observed for other Mo−Pt complexes containing a metal−metal bond. Mo−Pt distances of 2.912(4), 2.957(3), and 2.958(1) Å have been determined for $[MeCp(OC)_2Mo(\mu\text{-dppm})Pt(dppm)]^+$, the tetranuclear chain complex $[CpMoPt(H)(\mu\text{-}PPh_2)_2(CO)_2]_2$, and the cluster $[MoRhPt(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\sigma,\eta^2\text{-}C_6H_5)(PPh_3)(Cp)]$, respectively.[24] The overall geometry and ligand arrangement around the Mo center is reminiscent of **4b** and may be considered as distorted octahedral with an additional metal−metal bond bisecting the angle between C(4) and the sulfur atom [C(4)−Mo−S 102.1(2)°, C(4)−Mo−Pt 71.7(2)°, S−Mo−Pt 47.24(3)°]. The Pt atom is present in a distorted square planar environment (the rms deviation from the plane defined by Pt, Mo, P(2), P(3), and S being only 0.085 Å), thus conferring an 18-electron configuration for the Mo center and a 16-electron configuration for the Pt^0 center. The coordination polyhedra of the two metal fragments are again mutually inclined, which is manifested in the torsion angle P(1)−Mo−Pt−P(2) of 32.39° between the two dppa-phosphorus atoms. In addition to the spanning by the dppa backbone forming a five-membered ring, the two metal centers are asymmetrically bridged by a μ-SO_2 ligand via its sulfur atom. The Mo−S bond length of 2.531(2) Å is significantly longer than the Pt−S bond length of 2.220(1) Å. For comparison, a Mo−S bond length of 2.386(7) Å has been reported for $[(OC)_2Mo(\mu\text{-}CO)(\mu\text{-}SO_2)(\mu\text{-dppm})_2RhCl]$.[23a] The Pt−S distance is in the typical range found for SO_2-bridged platinum clusters.[25] In contrast to $[(OC)_2Mo(\mu\text{-}CO)(\mu\text{-}SO_2)(\mu\text{-dppm})_2RhCl]$, where somewhat different S−O distances [1.51(2) and (1.46(2) Å] have been observed, those of **7a** are almost identical (1.462(3) and 1.472(3) Å) (Figure 5).

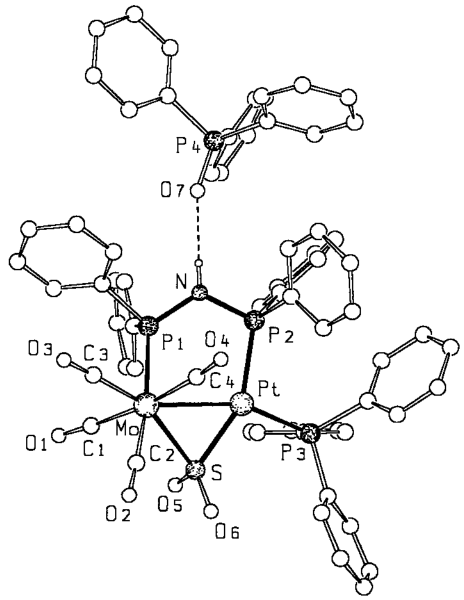

Figure 5. View of the crystal structure of $[(OC)_4Mo(\mu\text{-}SO_2)(\mu\text{-dppa})Pt(PPh_3)]\cdot O{=}PPh_3$ (**7a**) with the atom-numbering scheme.

Conclusion

We have shown that heterobimetallic dppa-bridged Mo−Pt and W−Pt complexes $[(OC)_4M(\mu\text{-}CO)(\mu\text{-dppa})Pt(PPh_3)]$ are easy accessible by reaction of the metallophosphines $[(OC)_5M(\eta^1\text{-dppa})]$ with $[Pt(C_2H_4)(PPh_3)_2]$. The reactivity of these μ-CO complexes toward various isonitriles has been investigated. Heterobimetallic μ-CNR complexes $[(OC)_4M(\mu\text{-}C{=}NR)(\mu\text{-dppa})Pt(PPh_3)]$ possessing an asymmetric isonitrile bridge can be obtained by selective substitution of a μ-CO ligand, if the incoming isonitrile behaves as a good π-acceptor. In the case of more electron-donating isonitriles, a terminal coordination of the CNR ligand is preferred to yield the very labile substitution products $[(OC)_3(RN{\equiv}C)M(\mu\text{-}CO)(\mu\text{-dppa})Pt(PPh_3)]$. We are currently investigating the reactivity of $[(OC)_4M(\mu\text{-}CO)(\mu\text{-}Ph_2PXPPh_2)Pt(PR_3)]$ and $[(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}Ph_2PXPPh_2)Pt(PR_3)]$ (X = NH, CH_2) toward other isonitriles possessing good π-acceptor properties to extend the still very limited number of

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Table 5. Summary of Crystal Data, Intensity Measurements, and Refinement of 1a and 2a

	1a	**2a**
empirical formula	$C_{31}H_{25}MoN_2O_5P_2$	$C_{30}H_{24}MoN_2O_4P_2$
formula mass, g mol^{-1}	663.41	634.39
collection T, K	293(2)	293(2)
λ(Mo Kα), pm	71.073	71.073
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, pm	1104.5(12)	1111.1(14)
b, pm	1213.0(12)	1452.3(14)
c, pm	1221.2(12)	1863(2)
α, deg	94.60(13)	90
β, deg	104.03(13)	104.3(2)
γ, deg	92.11(13)	90
V, pm^3	1.580(3)	2.913(5)
Z	2	4
D(calcd), g cm^{-3}	1.395	1.446
μ, mm^{-1}	0.556	0.597
F(000)	674	1288
cryst dimens, mm	0.60 × 0.30 × 0.30	0.50 × 0.40 × 0.30
diffractometer	Siemens Stoe AED 2	Siemens Stoe AED 2
θ range, deg	1.69–22.50	1.80–22.50
index ranges ($-h/h$, $-k/k$, $-l/l$)	$-11/11$, $-13/13$, 0/13	$-11/11$, 0/15, 0/20
no. of reflns colled	4122	3806
no. of indep reflns	4122	3806
no. of obs reflns [$I > 2\sigma(I)$]	3833	3337
no. of restraints/params	0/375	0/357
goodness of fit	1.101	1.107
$R1^a$ [$I > 2\sigma(I)$]	0.0272	0.0259
wR2^b(all data)	0.0698	0.0681
max/min res electron dens, e nm^{-3}	290/-430	230/-290

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

Table 6. Summary of Crystal Data, Intensity Measurements, and Refinement of 4b and 7a

	4b	**7a**
empirical formula	$C_{60}H_{57}N_2O_6P_3PtS\ W$	$C_{66}H_{55}Cl_4MoNO_7P_4PtS$
formula mass, g mol^{-1}	1405.99	1562.88
collection T, K	293(2)	293(2)
λ(Mo Kα), pm	71.073	71.073
cryst syst	orthorhombic	triclinic
space group	$Pbca$	$P\bar{1}$
a, pm	2055.0(13)	1254.4(3)
b, pm	2209.8(14)	1457.5(3)
c, pm	2605(2)	1920.0(4)
α, deg	90	99.78(3)
β, deg	90	98.99(3)
γ, deg	90	103.00(3)
V, pm^3	11.830(13)	3.3008(12)
Z	8	2
D(calcd), g cm^{-3}	1.579	1.572
μ, mm^{-1}	4.472	2.649
F(000)	5536	1556
cryst dimens, mm	0.40 × 0.30 × 0.20	0.50 × 0.40 × 0.30
diffractometer	Siemens Stoe AED 2	Siemens Stoe AED 2
θ range, deg	1.56–22.50	1.64–25.07
index ranges ($-h/h$, $-k/k$, $-l/l$)	0/12, 0/23, 0/28	$-14/14$, $-17/17$, 0/22
no. of reflns colled	5575	11 217
no. of indep reflns	5575	11 217
no. of obs reflns [$I > 2\sigma(I)$]	4500	10374
no. of restraints/params	0/649	0/771
goodness of fit	1.170	1.076
$R1^a$ [$I > 2\sigma(I)$]	0.0399	0.0343
wR2^b (all data)	0.1107	0.0921
max/min res electron dens, e nm^{-3}	940/-580	1655/-1725

[a] $R1 = \sum||F_o| - |F_c||/\sum | F_o |$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/ \sum[w(F_o^2)^2]\}^{0.5}$.

heterobimetallic μ-CNR complexes to further study their chemical reactivity and structural aspects in the crystalline state.

Experimental Section

All reactions were performed in Schlenk-tube flasks under purified nitrogen. Solvents were dried and distilled under nitrogen before use, toluene and hexane over sodium. Dichloromethane was distilled from P_4O_{10}. Nitrogen was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen or water. Elemental C, H, and N analyses were performed on a Leco Elemental Analyzer CHN 900. The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded at 200.13, 81.01, and 50.32 MHz, respectively, on a Bruker ACP 200 instrument. Phosphorus chemical shifts were referenced to 85% H_3PO_4 in H_2O with downfield shifts reported as positive. ^{195}Pt chemical shifts were measured on a Bruker ACP

200 instrument (42.95 MHz) and externally referenced to K$_2$PtCl$_4$ in water with downfield chemical shifts reported as positive. The numbering of the phosphorus nuclei in the ^{31}P NMR spectra corresponds to the numbering used in the single-crystal X-ray determinations. NMR spectra were recorded in pure CDCl$_3$, unless otherwise stated. The presence and amount of toluene of solvation in **3a**,**b** and of CH$_2$Cl$_2$ in **5a**,**b** have been determined from the ^{1}H NMR spectrum. The reactions were generally monitored by IR spectroscopy in the ν(CO) region. Tosylmethyl isonitrile, benzyl isonitrile, and 2,6-xylyl isonitrile were obtained from Aldrich and Fluka and used as received. Dppa was prepared as described by Meinel and Nöth.[13]

[(OC)$_5$Mo(η^1-dppa)] (1a). Me$_3$NO (0.751 g, 10.0 mmol) was added to a suspension of Mo(CO)$_6$ (2.64 g, 10.0 mmol) in 150 mL of MeCN. After stirring for 30 min, dppa (3.853 g, 10 mmol) was added to the clear yellow solution. The mixture was stirred for 3 h. The crude product containing ca. 10% of **2a** crystallized in a refrigerator at 5 °C. Suitable crystals for X-ray crystallography were separated manually. A second crop of pure **1a**·MeCN was precipitated as a colorless powder by addition of hexane to the mother liquor. After drying in vacuo for several hours the coordinated acetonitrile was removed. Overall yield: 5.34 g, 86%. Anal. Found: C, 55.50; H, 3.65; N, 2.32. Calcd for C$_{29}$H$_{21}$NO$_5$P$_2$Mo (M = 621.38): C, 56.05; H, 3.41; N, 2.25. IR (CH$_2$Cl$_2$) ν(CO): 2072 s, 1991 w, 1946 vs cm^{-1}. NMR: ^{1}H (298 K), δ 1.96 (s, 3H, MeCN), 3.86 (“t”, br, 1H, NH, ^2J(P−H = 7.1 Hz), 7.24−7.64 (m, 20H, phenyl); ^{31}P{^{1}H}, δ 83.9 (d, P^1(Mo), ^2J(P^1−P^2) = 65 Hz), 32.9 (d, P^2(uncoordinated).

[(OC)$_5$W(η^1-dppa)]·MeCN (1b). Me$_3$NO (0.751 g, 10.0 mmol) was added to a suspension of W(CO)$_6$ (3.51 g, 10.0 mmol) in a mixture of 100 mL of MeCN/50 mL of toluene. After stirring for 2 h, dppa (3.853 g, 10 mmol) was added to the clear yellow solution. The mixture was heated at 60 °C for 2 days. After filtration of some insoluble material a mixture of green-yellow **2b**·MeCN (80%) and nearly colorless **1b**·MeCN (20%) (^{31}P NMR integration) cocrystallized at 5 °C. A second crop of a mixture of **2b**·MeCN (15%) and **1b**·MeCN (85%) was obtained after layering the mother liquor with hexane. Pure **1b**·MeCN was isolated by separation of the resulting crystals by hand. Anal. Found: C, 50.14; H, 3.44; N, 3.72. Calcd for C$_{29}$H$_{21}$NO$_5$P$_2$W·MeCN (M = 709.29 + 41.05): C, 49.63, H, 3.22; N, 3.74. IR (CH$_2$Cl$_2$) ν(CO): 2071 s, 1980 w, 1937 vs cm^{-1}. NMR: ^{1}H (298 K), δ 1.94 (s, 3H, MeCN), 3.33 (“t”, br (not resolved dd), 1H, NH), 7.11−7.54 (m, 20H, phenyl); ^{31}P{^{1}H}, δ 63.7 (d, P^1(W), ^2J(P^1−P^2) = 59 Hz, ^1J(P−W) 192 Hz), 32.7 (d, P^2(uncoordinated).

[(OC)$_4$Mo(μ-CO)(μ-dppa)Pt(PPh$_3$)] (3a). [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] (0.748 g, 1.0 mmol) was added to a solution of **1a** (0.621 g, 1 mmol) in toluene (10 mL). Ethylene evolution was observed and the solution turned rapidly to yellow-orange. After 15 min precipitation of the bright yellow product occurred, which was completed by slow concentration of the solution under reduced pressure and subsequent addition of hexane (10 mL). The product was filtered off, rinsed with hexane, and dried under vacuum. ^{31}P NMR spectroscopy revealed that the crude product was contaminated with ca. 10% of the chelate complex [(OC)$_4$Mo(dppa)], **2a**. A second crop of analytically pure **3a** was obtained from the mother liquor after 3 days at 4 °C in the form of yellow microcystals, which contained one molecule of toluene of solvation. Overall yield: 0.954 g, 82%. Anal. Found: C, 54.98; H, 3.54; N, 1.45. Calcd for C$_{47}$H$_{36}$NO$_5$P$_3$PtMo·C$_7$H$_8$ (M = 1078.75 + 92.06): C, 55.39; H, 3.79.; N, 1.20. IR (KBr): ν(NH), 3320 w; (CH$_2$Cl$_2$) ν(CO), 2021 s, 1914 vs, br, 1890 sh, 1805 m, br cm^{-1}. NMR: ^{1}H, δ 4.89 (m, br, 1H, NH, ^3J(Pt−H) = 105 Hz), 6.89−7.69 (m, 35H, C$_6$H$_5$); ^{31}P{^{1}H}, δ 89.1 (dd, P^1(Mo), ^{2+3}J(P^1−P^2) = 157, ^{3+4}J(P^1−P^3) = 25, ^{2+3}J(Pt−P) = 69 Hz), 79.9 (dd, P^2(Pt), ^{2+3}J(P^1−P^2) = 157, ^2J(P^2−P^3) = 75, ^1J(P−Pt) = 3879 Hz), 42.8 (dd, P^3(Pt), ^2J(P^2−P^3) = 75, ^{3+4}J(P^1−P^3) = 25, ^1J(P−Pt) = 4089 Hz); ^{195}Pt{^{1}H}, δ −2676 (ddd, ^1J(Pt−P) = 4089, 3878, ^{2+3}J(Pt−P) = 69 Hz).

[(OC)$_4$W(μ-CO)(μ-dppa)Pt(PPh$_3$)] (3b). This complex was prepared as decribed for **3a**. Yield: 0.982 g, 81%. Anal. Found: C, 49.68; H, 3.41; N, 1.25. Calcd for C$_{47}$H$_{36}$NO$_5$P$_3$PtW·0.5C$_7$H$_8$ (M = 1166.66 + 46.03): C, 50.02; H, 3.33; N, 1.16. IR (CH$_2$Cl$_2$): ν(NH), 3318 w; ν(CO), 2018 s, 1908 vs, br, 1791 m, br cm^{-1}; NMR: ^{1}H, δ 5.37 (dt, br, 1H, NH, ^2J(P−H) = 9, ^4J(P−H) = 4, ^3J(Pt−H) = 106 Hz), 6.82−7.49 (m, 35H, C$_6$H$_5$); ^{31}P{^{1}H}, δ 79.1 (dd, P^2(Pt), ^{2+3}J(P^1−P^2) = 166, ^2J(P^2−P^3) = 73, ^1J(P−Pt) = 3734 Hz), 65.2 (dd, P^1(W), ^{2+3}J(P^1−P^2) = 166, ^{3+4}J(P^1−P^3) = 28, ^{2+3}J(Pt−P) = 63 Hz, ^1J(P−W) = 167), 44.8 (dd, P^3(Pt), ^2J(P^2−P^3) = 73, ^{3+4}J(P^1−P^3) = 28, ^1J(P−Pt) = 4199 Hz); ^{195}Pt{^{1}H}, δ −2656 (ddd, ^1J(Pt−P) = 4199, 3734, ^{2+3}J(Pt−P) = 63 Hz).

[(OC)$_4$Mo(μ-CNCH$_2$SO$_2$*p*-tolyl)(μ-dppa)Pt(PPh$_3$)] (4a). Solid *p*-tosylmethyl isonitrile (0.098 g, 0.50 mmol) was added to a solution of **3a** (0.585 g, 0.50 mmol) in 15 mL of CH$_2$Cl$_2$. After being stirred for 30 min, the solution was concentrated to ca. 10 mL, layered with pentane (ca. 10 mL), and stored at −25 °C. Yellow microcrystals of **4a** were formed, which were collected after 2 days and dried in vacuo. Yield: 0.392 g, 63%. Anal. Found: C, 53.36; H, 4.09; N, 2.35. Calcd for C$_{55}$H$_{45}$N$_2$MoO$_6$P$_3$PtS (M = 1245.98): C, 53.01; H, 3.64; N, 2.25. IR (CH$_2$Cl$_2$): ν(CO), 2022 s, 1914 vs, br, 1890 sh; ν(C═N), 1677 m, br cm^{-1}. NMR: ^{1}H, δ 4.89 (m, br, 1H, NH, ^3J(Pt−H) = 108 Hz), 6.89−7.69 (m, 35H, C$_6$H$_5$); ^{31}P{^{1}H}, δ 83.9 (dd, P^1(Mo), ^{2+3}J(P^1−P^2) = 131, ^{3+4}J(P^1−P^3) = 36, ^{2+3}J(Pt−P) = 59 Hz), 72.4 (dd, P^2(Pt), ^{2+3}J(P^1−P^2) = 131, ^2J(P^2−P^3) = 57, ^1J(P−Pt) = 3307 Hz), 41.8 (dd, P^3(Pt), ^2J(P^2−P^3) = 57, ^{3+4}J(P^1−P^3) = 36, ^1J(P−Pt) = 4481 Hz); ^{195}Pt{^{1}H}, δ −2671 (ddd, ^1J(Pt−P) = 4481, 3307, ^{2+3}J(Pt−P) = 59 Hz).

[(OC)$_4$W(μ-CNCH$_2$SO$_2$*p*-tolyl)(μ-dppa)Pt(PPh$_3$)] (4b). Solid *p*-tosylmethyl isonitrile (0.098 g, 0.50 mmol) was added to a solution of **3b** (0.606 g, 0.50 mmol) in 10 mL of CH$_2$Cl$_2$. After being stirred for 30 min, the solution was layered with pentane (ca. 15 mL) and stored at 5 °C in a refrigerator. Orange-red crystals of **4b** were formed, which were collected after 2 days. Yield: 0.349 g, 84%. Anal. Found: C, 51.40; H, 4.09; N, 2.04. Calcd for C$_{55}$H$_{45}$N$_2$O$_6$P$_3$PtSW·C$_5$H$_{12}$ (M = 1333.90 + 72.09): C, 51.25; H, 4.09; N, 1.99. IR (CH$_2$Cl$_2$): ν(NH), 3319 w; ν(CO), 2015 s, 1908 vs, br; ν(C═N), 1669 m cm^{-1}. NMR: ^{1}H, δ 2.26 (s, 3H, tolyl−CH$_3$), 4.86 (s, br, NCH$_2$), 5.32 (dt, br, 1H, NH, ^2J(P−H) = 8, ^4J(P−H) = 4, ^3J(Pt−H) = 88 Hz), 6.61−7.56 (m, 39H, phenyl); ^{31}P{^{1}H}, δ 71.2 (dd, P^2(Pt), ^{2+3}J(P^1−P^2) = 134, ^2J(P^2−P^3) = 56, ^1J(P−Pt) = 3253 Hz), 58.1 (dd, P^1(W), ^{2+3}J(P^1−P^2) = 134, ^{3+4}J(P^1−P^3) = 38, ^{2+3}J(Pt−P) = 49, ^1J(P−W) = 219 Hz), 43.7 (dd, P^3(Pt), ^2J(P^2−P^3) = 56, ^{3+4}J(P^1−P^3) = 39, ^1J(P−Pt) = 4448 Hz); ^{195}Pt{^{1}H}, δ −2682 (ddd, ^1J(Pt−P) = 4448, 3253, ^{2+3}J(Pt−P) = 49 Hz).

[(OC)$_4$Mo(μ-CN(H)CH$_2$SO$_2$p-tolyl)(μ-dppa)Pt(PPh$_3$)][BF$_4$] (5a). This complex was prepared by addition of an excess of HBF$_4$·Et$_2$O at 253 K to a solution of **4a** (0.125 g, 0.1 mmol) in CH$_2$Cl$_2$ (10 mL). After warming all volatiles were removed under reduced pressure. The orange-red residue was rinsed with Et$_2$O (3 mL) and dried again in vacuo. Yield: 0.104 g, 76%. Anal. Found: C, 48.13; H, 3.53; N, 1.94. Calcd for C$_{55}$H$_{46}$BF$_4$MoN$_2$O$_6$P$_3$PtS·0.5CH$_2$Cl$_2$ (M = 1333.80 + 42.46): C, 48.47; H, 3.37; N, 2.04. IR (CH$_2$Cl$_2$): ν(CO), 2054 s, 2006 m, 1957 vs, br; ν(C−N), 1519 w cm^{-1}. NMR: ^{1}H, δ 2.39 (s, 3H, tolyl−CH$_3$), 4.89 (d, br, NCH$_2$, ^4J(P−H) = 5.9 Hz), 6.11 (m, br, 1H, NH, ^3J(Pt−H) = 74 Hz), 6.51−7.64 (m, 39H, phenyl), 8.01 (m, br, 1H, CNH); ^{31}P{^{1}H}, δ 81.6 (dd, P^1(Mo), ^{2+3}J(P^1−P^2) = 81, ^{3+4}J(P^1−P^3) = 28, ^{2+3}J(Pt−P) = 132 Hz), 62.2 (dd, P^2(Pt), ^{2+3}J(P^1−P^2) = 81, ^2J(P^2−P^3) = 12, ^1J(P−Pt) = 2792 Hz), 38.6 (dd, P^3(Pt), ^2J(P^2−P^3) = 12, ^{3+4}J(P^1−P^3) = 28, ^1J(P−Pt) = 4086 Hz); ^{195}Pt{^{1}H} (258 K), δ −2392 (ddd, ^1J(Pt−P) = 4112, 2790, ^{2+3}J(Pt−P) = 132 Hz). ^{13}C{^{1}H} NMR: δ 22.0 (s, tolyl−*C*H$_3$), 75.1 (d, br, N−*C*H$_2$, ^4J(P−C) = 11 Hz), 127.5−146.1 (m, aromatic C), 204.3 (d, 2 CO, ^2J(P−C) = 9 Hz), 207.5 (d, 1 CO, ^2J(P−C) = 11 Hz), 208.1 (d, 1 CO, ^2J(P−C) = 18 Hz), 321.9 (dd, μ-C, ^2J(P−C) = 10, 66 Hz).

[(OC)$_4$W(*μ*-CN(H)CH$_2$SO$_2$p-tolyl)(*μ*-dppa)Pt(PPh$_3$)][BF$_4$] (5b). This orange-yellow complex was prepared in quantitative yield as described for **5a**. Anal. Found: C, 44.78; H, 3.47; N, 1.93. Calcd for $C_{55}H_{46}BF_4N_2O_6P_3PtSW\cdot CH_2Cl_2$ (M = 1421.71 + 84.94): C, 44.64; H, 3.21; N, 1.86. IR (CH_2Cl_2): ν(CO), 2052 s, 2001 m, 1951 vs, br; ν(C−N), 1515 m cm^{-1}. NMR: ^{1}H, δ 2.41 (s, 3H, tolyl−CH$_3$), 4.86 (d, br, NCH$_2$, ^4J(P−H) = 7.9 Hz), 6.82 (m, br, 1H, NH), 6.57−7.55 (m, 39H, phenyl), 7.83 (m, br, 1H, CNH); ^{31}P{^{1}H}, δ 59.6 (dd, P^2(Pt), ^{2+3}J(P^1−P^2) = 72, ^2J(P^2−P^3) = 6, ^1J(P−Pt) = 2767 Hz), 52.5 (dd, P^1(W), ^{2+3}J(P^1−P^2) = 72, ^{3+4}J(P^1−P^3) = 23, ^{2+3}J(Pt−P) = 97 Hz, ^1J(P−W) = 222 Hz), 40.0 (dd, P^3(Pt), ^2J(P^2−P^3) = 6, ^{3+4}J(P^1−P^3) = 23, ^1J(P−Pt) = 4217 Hz); ^{195}Pt{^{1}H}; δ −2385 (ddd, ^1J(Pt−P) = 4217, 2767, ^{2+3}J(Pt−P) = 97 Hz). ^{13}C{^{1}H} NMR: δ 21.6 (s, tolyl−*C*H$_3$), 75.3 (d, br, N−*C*H$_2$, ^4J(P−C) = 15 Hz), 128.1−146.6 (m, aromatic C), 195.2 (d, 2 CO, ^2J(P−C) = 8 Hz), 197.5 (d, 1 CO, ^2J(P−C) = 15 Hz), 199.3 (d, 1 CO, ^2J(P−C) = 9 Hz), 318.5 (dd, *μ*-C, ^2J(P−C) = 9, 68 Hz).

[(OC)$_3$(xylylNC)W(*μ*-CN(H)CH$_2$SO$_2$*p*-tolyl)(*μ*-dppa)Pt(PPh$_3$)][BF$_4$] (6a). This complex was prepared by addition of 2,6-xylylNC (0.131 g, 0.1 mmol) to a solution of **5b** (0.151 g, 0.1 mmol) in CH_2Cl_2 (9 mL). After stirring for 3 h, the volume was reduced to ca. 5 mL and the solution layered with Et_2O. After 2 days in a refrigerator yellow-orange crystals were formed, which were dried in vacuo for several hours. Yield: 0.10 g, 69%. Anal. Found: C, 49.76; H, 3.88; N, 2.68. Calcd for $C_{63}H_{55}BF_4N_3O_5P_3PtSW$ (M = 1524.87): C, 49.62; H, 3.64; N, 2.75. IR (CH_2Cl_2): ν(CN), 2136 s; ν(CO), 2018 m, 1938 vs; ν(C=N), 1596 w cm^{-1}. NMR: ^{1}H, δ 1.99 (s, 6H xylyl−CH$_3$), 2.40 (s, 3H, tolyl-CH$_3$), 4.84 (d, br, 2H, NCH$_2$, ^4J(P−H) = 6.2 Hz), 6. 44 (m, br, 1H, NH, ^3J(Pt−H) = 84 Hz), 6.53−7.60 (m, 39H, phenyl), (CNH not observed); ^{31}P{^{1}H}, δ 61.8 (dd, P^2(Pt), ^{2+3}J(P^1−P^2) = 79, ^2J(P^2−P^3) = 11, ^1J(P−Pt) = 2869 Hz), 58.3 (dd, P^1(W), ^{2+3}J(P^1−P^2) = 79, ^{3+4}J(P^1−P^3) = 31, ^{2+3}J(Pt−P) = 144 Hz), 39.8 (dd, P^3(Pt), ^2J(P^2−P^3) = 11, ^{3+4}J(P^1−P^3) = 31, ^1J(P−Pt) = 3954 Hz); ^{195}Pt{^{1}H}, δ −2459 (ddd, ^1J(Pt−P) = 3954, 2869, ^{2+3}J(Pt−P) = 144 Hz). ^{13}C{^{1}H} NMR: δ 18.2 (s, xylyl−*C*H$_3$), 21.6 (s, tolyl-*C*H$_3$), 74.9 (d, br, N−*C*H$_2$, ^4J(P−C) = 12 Hz), 127.9−147.2 (m, aromatic C), 155.1 (d, *C*N, ^2J(P−C) = 10 Hz), 198.6 (dd, 2 CO, ^2J(P−C) = 2, 9 Hz), 200.6 (d, 1 CO, ^2J(P−C) = 20 Hz), 314.7 (ddd, *μ*-C, ^2J(P−C) = 3, 6, 66 Hz).

[(OC)$_3$(benzylNC)W(*μ*-CN(H)CH$_2$SO$_2$*p*-tolyl)(*μ*-dppa)Pt(PPh$_3$)][BF$_4$] (6b). This complex was prepared as described for **6a**. Due to the formation of some Ph$_3$P=O during attempts to obtain single crystals, no satisfactory elemental analysis could be obtained. The FAB$^+$ mass spectrum (NBA matrix) displays an intense peak for the cationic fragment at *m*/*z* 1424 (55%), whose simulated isotopic distribution is in agreement with the experimental pattern. IR (CH_2Cl_2): ν(CN), 2156 m, ν(CO) 2020 m, 1939 vs; ν(C=N), 1598 w cm^{-1}. NMR: ^{1}H, δ 2.46 (s, 3H, tolyl−CH$_3$), 4, 39 (s,br, 2H, benzyl−CH$_2$), 4.84 (d, br, 2H, NCH$_2$, ^4J(P−H) = 6.1 Hz), 6. 41 (m, br, 1H, NH, ^3J(Pt−H) = 89 Hz), 6.53−7.60 (m, 44H, phenyl), (CNH not observed); ^{31}P{^{1}H}, δ 61.1 (dd, P^2(Pt), ^{2+3}J(P^1−P^2) = 81, ^2J(P^2−P^3) = 12, ^1J(P−Pt) = 2874 Hz), 58.1 (dd, P^1(W), ^{2+3}J(P^1−P^2) = 81, ^{3+4}J(P^1−P^3) = 32, ^{2+3}J(Pt−P) = 147 Hz), 39.1 (dd, P^3(Pt), ^2J(P^2−P^3) = 12, ^{3+4}J(P^1−P^3) = 32, ^1J(P−Pt) = 3908 Hz).

[(OC)$_4$Mo(*μ*-SO$_2$)(*μ*-dppa)Pt(PPh$_3$)]·Ph$_3$P=O (7a). A solution of **3a** (0.585 g, 0.50 mmol) in 10 mL of CH_2Cl_2 was purged with a slow stream of SO_2 for 10 min. After stirring for 15 min, an equimolar amount of Ph$_3$P=O was added and the solution concentrated to ca. 10 mL, layered with hexane (ca. 10 mL), and stored at −25 °C. Yellow-orange microcrystals of **7a**·Ph$_3$P=O were formed, which were collected after 2 days and dried in vacuo for 12 h to remove the solvated dichloromethane. Yield: 0.550 g, 79%. Anal. Found: C, 54.86; H, 3.49; N, 0.97. Calcd for $C_{64}H_{51}NMoO_7P_4PtS$ (M = 1393.10): C, 55.18; H, 3.69; N, 1.00. IR (KBr): ν(CO), 2032 s, 1927 vs, br; ν(SO), 1180 m, 1043 m cm^{-1}. NMR: ^{1}H, δ 5.71 (m, br, 1H, NH, ^3J(Pt−H) = 119 Hz), 6.89−7.69 (m, 50H, C$_6$H$_5$); ^{31}P{^{1}H}, δ 86.2 (dd, P^1(Mo), ^{2+3}J(P^1−P^2) = 123, ^{3+4}J(P^1−P^3) = 26, ^{2+3}J(Pt−P) = 24 Hz), 66.9 (dd, P^2(Pt), ^{2+3}J(P^1−P^2) = 123, ^2J(P^2−P^3) = 36 ^1J(P−Pt) = 3745 Hz), 29.3 (s, Ph$_3$PO), 27.4 (dd, P^3(Pt), ^2J(P^2−P^3) = 36, ^{3+4}J(P^1−P^3) = 26, ^1J(P−Pt) = 4551 Hz).

[(OC)$_4$W(*μ*-SO$_2$)(*μ*-dppa)Pt(PPh$_3$)] (7b). A solution of **3b** (0.606 g, 0.50 mmol) in 10 mL of CH_2Cl_2 in 10 mL of CH_2Cl_2 was purged with a slow stream of SO_2 for 10 min. After stirring for 20 min. the solution was concentrated to ca. 10 mL, layered with hexane (ca. 10 mL), and stored at −25 °C. Yellow-orange microcrystals of **7b** were formed, which were collected after 2 days and dried in vacuo for 10 h. Yield: 0.433 g, 72%. Anal. Found: C, 46.40; H, 3.46; N, 1.45. Calcd for $C_{46}H_{36}NO_6P_3PtWS$ (M = 1202.72): C, 45.94; H, 3.02; N, 1.17. IR (CH_2Cl_2): ν(CO), 2043 s, 1956 sh, 1942 vs cm^{-1}. NMR: ^{1}H, δ 5.71 (m, br, 1H, NH, ^3J(Pt−H) = 119 Hz), 6.89−7.69 (m, 50H, C$_6$H$_5$); ^{31}P{^{1}H}, δ 67.4 (dd, P^2(Pt), ^{2+3}J(P^1−P^2) = 130, ^2J(P^2−P^3) = 32, ^1J(P−Pt) = 3712 Hz), 59.1 (dd, P^1(W), ^{2+3}J(P^1−P^2) = 130, ^{3+4}J(P^1−P^3) = 26, ^{2+3}J(Pt−P) = 4 Hz), 28.3 (dd, P^3(Pt), ^2J(P^2−P^3) = 32, ^{3+4}J(P^1−P^3) = 26, ^1J(P−Pt) = 4307 Hz).

X-ray Crystal Structure Determinations. The crystals were placed in a glass capillary and then mounted on a Siemens Stoe AED2 diffractometer. Cell parameters were obtained from least-squares fits to the settings of 25 reflections in the range 5° < 2θ < 25°. No significant deviations in intensity were registered for three monitored reflections recorded at regular intervals. An empirical absorption correction was applied by ψ-scans. The structure was solved by direct methods.[26] The positions of all non-hydrogen atoms were refined anisotropically.[27] A riding model was employed for the refinement of the C*H* hydrogen atom positions. The positions of the N*H* hydrogen atoms were localized in difference Fourier syntheses and refined freely. In **4b** a phenyl group bonded to P(2), the *p*-tolyl group, and a pentane molecule were found to be disordered. Crystallographic details are given in Tables 5 and 6.

Acknowledgment. The Deutsche Forschungsgemeinschaft is gratefully thanked for habilitation grants and financial support to M.K. and C.S. and the DEGUSSA AG for a generous gift of Pt salts. M.K. is also indebted to Prof. M. Veith and Dr. P. Braunstein for their support and for providing the institute facilities and to Dr. V. Huch for collection of the X-ray data sets.

Supporting Information Available: ORTEP drawings, tables of final atomic coordinates, tables of hydrogen atom coordinates, thermal parameters for the non-hydrogen atoms, and complete lists of bond distances and angles (40 pages). Ordering information is given on any current masthead page.

OM980756V

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